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Process Design for Dilute-Acid Pretreatment of Hardwood and Herbaceous Biomass Feedstock

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TASK 1: MODELING OF PERCOLATION PROCESS IN DILUTE-ACID HYDROLYSIS OF HYPRID POPLAR HEMICELLULOSE

Introduction

Dilute acid treatment of biomass is one of the common methods used for pretreatment of bioconversion. This method provides an additional benefit of hydrolyzing the hemicellulose fraction during the process. In the design of this process, therefore, it is essential to consider the production of hemicellulose sugar as well as the effectiveness of the pretreatment. From the viewpoint of sugar production, the treatment condition, type of reactor, and mode of reactor operation are important factors in the overall process. Previous studies at Auburn University (1-3) have established that the percolation reactor (packed-bed flow-through type) is one of the reactor types most suitable for biomass pretreatment. In the operation of this reactor, the sugar product is removed from the reactor as it is formed. This enables the process to attain high sugar yield by minimizing the sugar decomposition. Furthermore, the sugar product from a packed-bed type reactor is obtained at a high concentration level due to the high solid-to-liquid ratio that prevails in such a reactor.

In this research we have studied the use of this reactor in pretreatment/ hydrolysis of hemicellulose of hybrid poplar, a fast-growing (short rotation) hardwood. At the present time, it is considered one of the most promising biomass resources in the United States. The hemicellulose in hardwood species is known to be biphasic (4-9). That is, it is composed of two different fragments (a fast hydrolyzing fraction and a slow hydrolyzing fraction). The biphasic nature of substrate brings about a number of interesting points concerning the reactor design and operation, especially with regard to the temperature policy and the flow configuration in the reactor system.

This study was undertaken to see if there is theory to support any benefits from non-uniform temperature policy and from unconventional flow arrangements in percolation process, and if so, to verify their impacts on the performance of this reactor and to broaden the scope of the modeling investigation to other hardwoods.

In addition, the adverse effect due to non-ideal behavior of the reactor, especially the effect of intraparticle diffusion was studied. Also, the kinetic pattern was generalized by theoretical inclusion of xylo-oligomer.

Model Development

We have developed base, diffusion, and oligomer models. Each model was developed from different assumptions. In the base model diffusion effects were neglected and xylo-oligomer was not included in the model. In the diffusion model the effect of intraparticle sugar diffusion on yield was taken into account. And in the oligomer model the

formation of soluble xylo-oligomer as a recognizable product was considered. The following three sections explain how to develop the yield and concentration equation in each model.

1) Base Model

A simplistic description of a percolation reactor is given in Figure 1. The following assumptions are made in the modeling procedure:
1) The hemicellulose in hybrid poplar is composed of fast and slow hydrolyzing fragments.
2) Its kinetics follow the parallel consecutive first-order reactions:
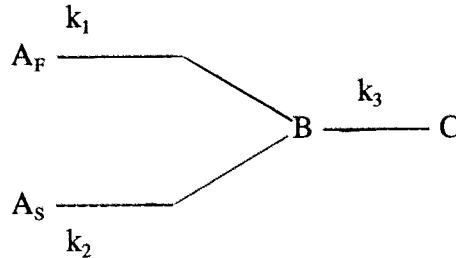
where A_F and A_S are fast and slow hemicellulose, respectively; B is xylose; and C is the decomposed product.
3) The axial heat transfer after temperature step-change is negligible.
4) The effect of diffusion in the reaction is negligible.

Material Balance

A material balance ovHx an incremental column height on component B leads to the

following:

$$u(\frac{\partial C_B}{\partial x})+k_3 C_B-k_1 C_{AF}-k_2 C_{AS}--(\frac{\partial C_B}{\partial t}) \qquad (1)$$

where

$$C_{AF}-C_{AF_o}e^{-k_1(t-\frac{x}{u})}, \quad t > \frac{x}{u},$$
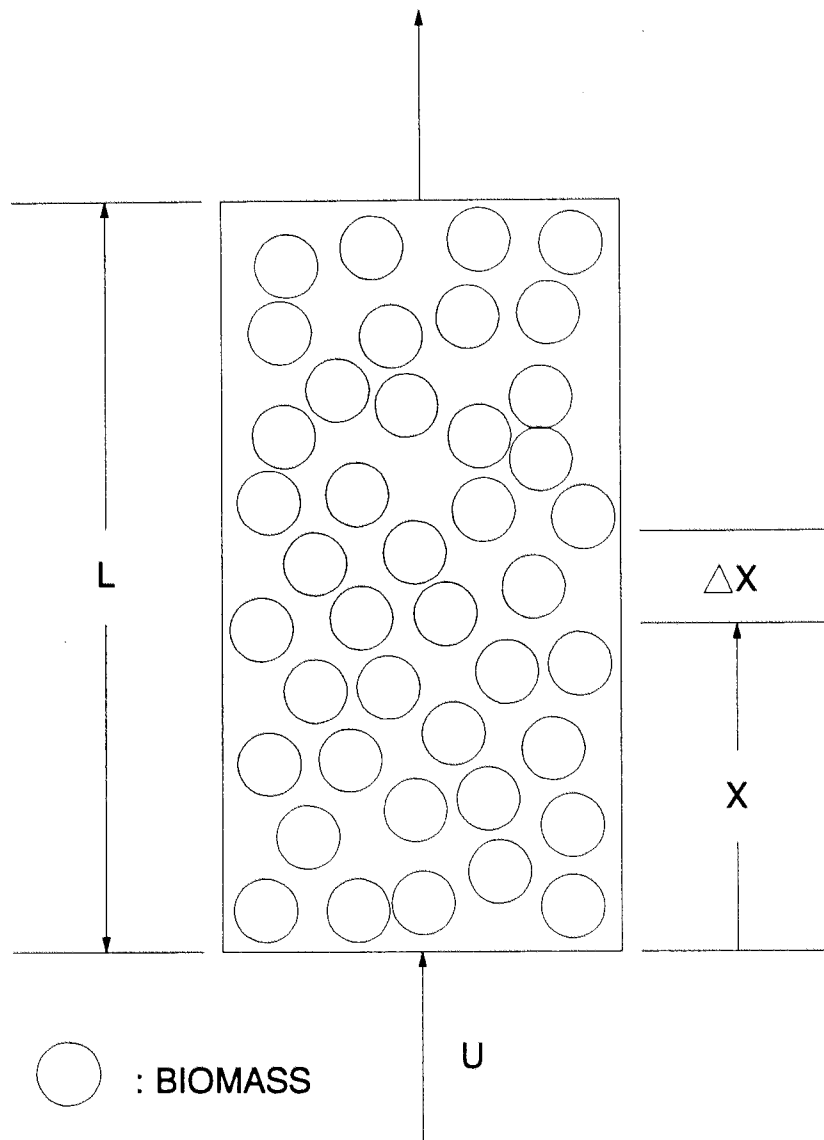
Figure 1.   Conceptual Sketch of Percolation Reactor

and

$$C_{AS} = C_{AS_o} e^{-k_2(t-\frac{x}{u})}, \quad t > \frac{x}{u}.$$

The pertinent initial and boundary conditions are:

$$x=0, \quad C_B=0 \qquad (2)$$

$$t=0, \quad C_B=0. \qquad (3)$$

In order to apply the principle of superposition, we let $C_B = C_{BF} + C_{BS}$, where C_{BF} represents sugar released from the fast fraction, and C_{BS} represents sugar released from the slow fraction. The above equations can be divided into two sets of equations with appropriate initial conditions and boundary conditions. Both sets of equations have the same form except for different coefficients. The equation regarding fast hemicellulose is:

$$u(\frac{\partial C_{BF}}{\partial x}) + k_3 C_{BF} - k_1 C_{AF} = -(\frac{\partial C_{BF}}{\partial t}), \qquad (4)$$

where

$$C_{AF} = C_{AF_o} e^{-k_1(t-\frac{x}{u})}, \quad t > \frac{x}{u}.$$

The equation for slow hemicellulose is:

$$u(\frac{\partial C_{BS}}{\partial x}) + k_3 C_{BS} - k_2 C_{AS} = -(\frac{\partial C_{BS}}{\partial t}), \qquad (5)$$

where

$$C_{AS} = C_{AS_o} e^{-k_1(t-\frac{x}{u})}, \quad t > \frac{x}{u}.$$

The boundary and initial conditions are the same as equation (2), (3).

Yield, Concentration and Optimum Conditions for Single Temperature Operation

By the Laplace transform method, one obtains the solution for equations (4) and (5) as follows:

$$S_{BF} = \frac{1}{\alpha_F} e^{\beta_F(z-\tau)}(1 - e^{(-\alpha_F\beta_F)z}), \qquad (6)$$

$$S_{BS} = \frac{1}{\alpha_S} e^{\beta_S(z-\tau)}(1 - e^{(-\alpha_S\beta_S)z}). \qquad (7)$$

Addition of equations (6) and (7) (superposition) yields the solution for the original partial differential equation of equations (1)-(3):

$$S_B = H_F S_{BF} + H_S S_{BS}. \qquad (8)$$

With regard to the reactor performance there are two items of vital interest, namely the yield and the product concentration. These are obtained from the solution. The yield for fast hemicellulose is:

$$Y_{BF} = \int_1^{\tau+1} (S_{BF})_{z-1} d\tau = \frac{(1 - e^{-\alpha_F\beta_F})}{\alpha_F\beta_F}(1 - e^{-\beta_F\tau}) \qquad (9)$$

The yield for slow hemicellulose is:

$$Y_{BS} = \int_1^{\tau+1} (S_{BS})_{z-1} d\tau = \frac{(1 - e^{-\alpha_S\beta_S})}{\alpha_S\beta_S}(1 - e^{-\beta_S\tau}) \qquad (10)$$

The combined yield is:

$$Y_B = H_F Y_{BF} + H_S Y_{BS} \qquad (11)$$

Average product concentration(C_P) can be expressed as follows:

$$C_P - C_{A_o} \frac{Yield}{\tau} \qquad (12)$$

where

$$C_{A_o} - \frac{total\ xylan\ as\ a\ xylose\ inside\ the\ percolation\ reactor}{total\ liquid\ volume\ inside\ the\ percolation\ reactor}$$

$$- \frac{(1-\varepsilon)(1-\theta)d_{cw}(\%\ xylan\ of\ hybrid\ poplar)}{(\varepsilon+(1-\varepsilon)\theta)0.88} \approx 3.471\%(w/v) \qquad (13)$$

The yield is now expressed as a function of reaction time and a number of dimensionless

parameters including β_F ($=k_1 L/u$).

Since β_F is an important adjustable parameter, it would be of interest to maximize

the yield with respect to β_F, as follows:

$$(\frac{\partial Y_B}{\partial \beta_F})_{\alpha,\tau} - (\frac{\partial Y_B}{\partial \beta_F})_{\alpha,\tau,\beta_S} + (\frac{\partial Y_B}{\partial \beta_S})_{\alpha,\tau,\beta_F}(\frac{\partial \beta_S}{\partial^-_F}) , -0 \qquad (14)$$

Equation (14) provides an implicit equation from which the optimum β_F and

consequently the corresponding maximum yield are determined.

Yield for Temperature Step Change Operation

The term τ_1 represents the dimensionless time up to the temperature shifting point. τ_2

represents the rest of the time period:

$$\tau - \tau_1 + \tau_2. \qquad (15)$$

We further define f such that

$$f - \frac{\tau_1}{\tau}. \qquad (16)$$

Total yield consists of four parts; namely, fast fraction reacting for duration of τ_1, slow for τ_1, fast for τ_2, and slow for τ_2.

The total yield is then expressed as:

$$Y_{BSTEP} - H_F(Y_{BF1} + R_{AF} Y_{BF2}) + H_S(Y_{BS1} + R_{AS} Y_{BS2}) \qquad (17)$$

where

$$Y_{BF1} - \int_1^{\tau_1+1} (S_{BF})_{z-1} d\tau - \frac{(1-e^{-\alpha_{F_1}\beta_{F_1}})}{\alpha_{F_1}\beta_{F_1}}(1-e^{-\beta_{F_1}\tau_1}), \qquad (18)$$

$$Y_{BS1} - \int_1^{\tau_1+1} (S_{BS})_{z-1} d\tau - \frac{(1-e^{-\alpha_{S_1}\beta_{S_1}})}{\alpha_{S_1}\beta_{S_1}}(1-e^{-\beta_{S_1}\tau_1}), \qquad (19)$$

$$Y_{BF2} - \int_1^{\tau_2+1} (S_{BF})_{z-1} d\tau - \frac{(1-e^{-\alpha_{F_2}\beta_{F_2}})}{\alpha_{F_2}\beta_{F_2}}(1-e^{-\beta_{F_2}\tau_2}), \qquad (20)$$

$$Y_{BS2} - \int_1^{\tau_2+1} (S_{BS})_{z-1} d\tau - \frac{(1-e^{-\alpha_{S_2}\beta_{S_2}})}{\alpha_{S_2}\beta_{S_2}}(1-e^{-\beta_{S_2}\tau_2}), \qquad (21)$$

$$R_{AF} \sim e^{-\beta_{FI}\tau_1}, \qquad (22)$$

$$R_{AS} \sim e^{-\beta_{SI}\tau_1}. \qquad (23)$$

The concentration and the optimum condition(β_F, β_S) can be determined in the same manner as in the uniform temperature operation.

2) Diffusion Model

To account for the effect of sugar component diffusion, one needs to set up the PDE's separately for the solid part and liquid part.

Material Balance Within Solid

The material balance on component B within the solid feed yields the equation:

$$D_e \frac{\partial^2 C_B}{\partial y^2} + k_1 C_{AF} + k_2 C_{AS} - k_3 CB - \frac{\partial C_B}{\partial t}, \qquad (24)$$

$$C_{BA} - \frac{1}{b} \int_o^b C_B \, dy. \qquad (25)$$

Material Balance Within Liquid

A material balance on component B which considers the liquid that exists both inside and outside of solid particles leads to the following:

$$-\epsilon u \frac{\partial C_{BL}}{\partial x} + (1-\epsilon)\theta k_1 C_{AF} + (1-\epsilon)\theta k_2 C_{AS} - k_3(\epsilon C_{BL} + (1-\epsilon)\theta C_{BA})$$

$$- \, \epsilon \frac{\partial C_{BL}}{\partial t} + (1-\epsilon)\theta \frac{\partial C_{BA}}{\partial t} \qquad (26)$$

By the principle of superposition, the above equations were divided into two sets of equations. Then each set was solved by Laplace Transform Method. The yield is expressed

as:

$$Y_{BSTEP} \, = \, H_F(Y_{BF1} + R_{AF}Y_{BF2}) \, + \, H_S(Y_{BS1} + R_{AS}Y_{BS2}) \qquad (27)$$

where

$$Y_{BF1} = \eta \frac{(1-e^{-\alpha'_{F_1}\beta_{F_1}})}{\alpha'_{F_1}\beta_{F_1}}(1-e^{-\beta_{F_1}\tau_1}),$$

$$Y_{BS1} = \eta \frac{(1-e^{-\alpha'_{S_1}\beta_{S_1}})}{\alpha'_{S_1}\beta_{S_1}}(1-e^{-\beta_{S_1}\tau_1}),$$

$$Y_{BF2} = \eta \frac{(1-e^{-\alpha'_{F_2}\beta_{F_2}})}{\alpha'_{F_2}\beta_{F_2}}(1-e^{-\beta_{F_2}\tau_2}),$$

$$Y_{BS2} = \eta \frac{(1-e^{-\alpha'_{S_2}\beta_{S_2}})}{\alpha'_{S_2}\beta_{S_2}}(1-e^{-\beta_{S_2}\tau_2}),$$

$$R_{AF} = e^{-\beta_{F_1}\tau_1},$$

$$R_{AS} - e^{-\beta_{s_1}\tau_1}.$$

It is noteworthy that when $\eta = 1$ and $p = 0$, the temperature step-change yield equation in the diffusion model reduces to equation (17) in the base model.

3) Oligomer Model

The PDEs (partial differential equations) of the M.B. (material balance) for xylo-oligomer and xylose in a percolation reactor were set up and were solved analytically. The overall kinetic model including soluble polysaccharide term, is expressed as:

$$H_F \xrightarrow{\quad k_1 \quad}$$
$$\xrightarrow{\qquad} \text{Xylo-oligomer} \xrightarrow{\quad k_4 \quad} \text{Xylose} \xrightarrow{\quad k_3 \quad} \text{Decomposed Product}$$
$$H_S \xrightarrow{\quad k_2 \quad}$$
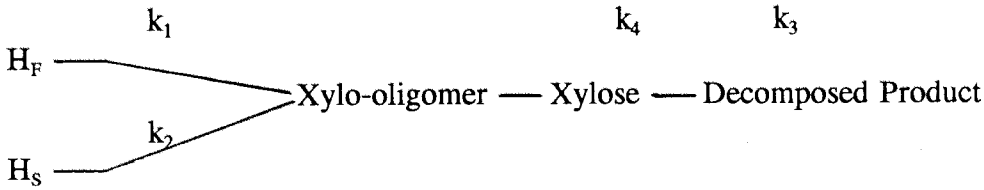
The solution for xylo-oligomer was obtained by solving the M.B. for xylo-oligomer. And the solution for xylose monomer was obtained by solving the M.B. for xylo-oligomer and the M.B. for xylose sequentially.

Material balance for soluble xylo-oligomer released from H_F leads to the following equation with dimensionless parameters:

$$\frac{\partial S_{oliF}}{\partial z} + \gamma_F \beta_F S_{oliF} - \beta_F e^{-\beta_F(\tau-z)} = -\frac{\partial S_{oliF}}{\partial \tau} \qquad (28)$$

The solution for xylo-oligomer is expressed as:

$$S_{oliF} - \frac{1}{\gamma_F} e^{\beta_F(z-\tau)}(1 - e^{-\gamma_F \beta z}) \qquad (29)$$

The yield for xylo-oligomer is expressed as:

$$Y_{oliF} - \int_1^{\tau+1} (S_{oliF})_{z-1} d\tau - \frac{(1 - e^{-\gamma_F \beta_F})}{\gamma_F \beta_F}(1 - e^{-\beta_F \tau}) \qquad (30)$$

Material balance for xylose released from H_F

$$\frac{\partial S_{BF}}{\partial z} + \alpha_F \beta_F S_{BF} - \gamma_F \beta_F S_{oliF} - -\frac{\partial S_{BF}}{\partial \tau} \tag{31}$$

Substitution of Eqn. 2 into Eqn. 4 yields the following equation.

$$\frac{\partial S_{BF}}{\partial z} + \alpha_F \beta_F S_{BF} - \beta_F e^{-\beta_F(\tau-z)}(1-e^{-\gamma_F\beta_F z}) - -\frac{\partial S_{BF}}{\partial \tau} \tag{32}$$

The solution for xylose is expressed as:

$$S_{BF}(\tau,z) - \frac{e^{\beta_F z}(e^{-\beta_F \tau} - e^{-\beta_F(1+\gamma_F)\tau})}{\alpha_F}$$

$$- \frac{e^{\beta_F \alpha_F}(e^{-\beta_F(\tau-z)} - e^{-\beta_F(1+\alpha_F)(\tau-z)})}{\alpha_F}$$

$$+ \frac{-e^{\beta_F(1-\gamma_F)z - \beta_F \tau} + e^{-\alpha_F \beta_F z - \beta_F(\tau-z)}}{\alpha_F - \gamma_F} \tag{33}$$

The xylose yield is expressed as:

$$Y_{BF} - \int_1^{\tau+1}(S_{BF})_{z-1}d\tau - \frac{e^{\beta_F}}{\alpha_F}[\frac{e^{-\beta_F(\tau+1)} - e^{\beta_F}}{-\beta_F} + \frac{e^{-\beta_F(1+\alpha_F)(\tau+1)} - e^{-\beta_F(1+\alpha_F)}}{\beta_F(1+\alpha_F)}]$$

$$-\frac{e^{\beta_F \alpha_F}}{\alpha_F}(\frac{e^{-\beta_F \tau}-1}{-\beta_F} - \frac{e^{-\beta_F(1+\alpha_F)\tau}-1}{\beta_F(1+\alpha_F)})$$

$$+\frac{e^{\beta_F(1-\alpha_F)}-e^{\beta_F(1-\gamma_F)}}{\alpha_F-\gamma_F}[\frac{e^{-\beta_F(\tau+1)}-e^{\beta_F}}{-\beta_F}] \qquad (34)$$

The derivation of the xylo-oligomer and xylose yield released from H_S is similar to that of the xylo-oligomer and xylose yield released from H_F. The yield of xylo-oligomer and xylose released from H_s is expressed as follows:

$$S_{olis} = \frac{1}{\gamma_S}e^{\beta_S(z-\tau)}(1-e^{-\gamma_S \beta z}) \qquad (35)$$

$$Y_{olis} = \int_1^{\tau+1}(S_{olis})_{z-1}d\tau = \frac{(1-e^{-\gamma_S \beta_S})}{\gamma_S \beta_S}(1-e^{-\beta_S \tau}) \qquad (36)$$

$$S_{BS}(\tau,z) = \frac{e^{\beta_S z}(e^{-\beta_S \tau}-e^{-\beta_S(1+\gamma_S)\tau})}{\alpha_S}$$

$$-\frac{e^{\beta_S \alpha_S}(e^{-\beta_S(\tau-z)}-e^{-\beta_S(1+\alpha_S)(\tau-z)})}{\alpha_S}$$

$$+\frac{-e^{\beta_S(1-\gamma_S)z-\beta_S \tau}+e^{-\alpha_S \beta_S z-\beta_S(\tau-z)}}{\alpha_S-\gamma_S} \qquad (37)$$

Xylose yield is expressed as:

$$Y_{BS} = \int_1^{\tau+1} (S_{BS})_{z-1} d\tau = \frac{e^{\beta_S}}{\alpha_S} \left[\frac{e^{-\beta_S(\tau+1)} - e^{\beta_S}}{-\beta_S} + \frac{e^{-\beta_S(1+\alpha_S)(\tau+1)} - e^{-\beta_S(1+\alpha_S)}}{\beta_S(1+\alpha_S)} \right]$$

$$- \frac{e^{\beta_S \alpha_S}}{\alpha_S} \left(\frac{e^{-\beta_S \tau} - 1}{-\beta_S} - \frac{e^{-\beta_S(1+\alpha_S)\tau} - 1}{\beta_S(1+\alpha_S)} \right)$$

$$+ \frac{e^{\beta_S(1-\alpha_S)} - e^{\beta_S(1-\gamma_S)}}{\alpha_S - \gamma_S} \left[\frac{e^{-\beta_S(\tau+1)} - e^{\beta_S}}{-\beta_S} \right] \qquad (38)$$

The total yield in uniform temperature is defined as the sum of xylo-oligomer yield and xylose yield. The total yield is expressed as:

$$Y_T(uniform\ temp) = H_F(Y_{oliF} + Y_{BF}) + H_S(Y_{oliF} + Y_{BS}) \qquad (39)$$

The definition of the total yield in temperature step-change is similar to that in the simple model, which is expressed as:

$$Y_T(step) = H_F[Y_{oliF1} + Y_{BF1} + R_{AF}(Y_{oliF2} + Y_{BF2})] + H_S[Y_{oliS1} + Y_{BS1} + R_{AS}(Y_{oliS2} + Y_{BS2})] \qquad (40)$$

4) Numerical Approach

A numerical solution was also sought for the governing PDE of the percolation reactor in order to accommodate a flexible reactor operation in which an analytical solution is unwieldy. In so doing, the dimensionless form of equation (4) was expressed as follows:

The dimensionless boundary and initial conditions are:

$$\left(\frac{\partial S}{\partial z}\right) + \alpha \beta S - \beta e^{-\beta(\tau - z)} = -\left(\frac{\partial S}{\partial z}\right). \qquad (41)$$

$$z=0, \; S=0, \qquad (42)$$

$$\tau=0, \; S=0. \qquad (43)$$

The finite difference method was applied to solve the PDE. The backward difference method for position (z-direction) and the forward difference method for time (τ-direction) were applied in conjunction with the given boundary and initial conditions, respectively. Equations (44) and (45) are the backward difference equation for position and the forward difference equation for time, respectively:

$$\left(\frac{\partial S}{\partial z}\right) = \frac{S_{i,n} - S_{i-1,n}}{\Delta z}, \qquad (44)$$

$$\left(\frac{\partial S}{\partial \tau}\right) = \frac{S_{i,n+1} - S_{i,n}}{\Delta \tau}. \qquad (45)$$

Substituting equation (44) and (45) into equation (41) yields:

$$\frac{S_{i,n} - S_{i-1,n}}{\Delta z} + \alpha \beta S_{i,n} - \beta e^{-\beta(\tau_n - z_i)} = -\frac{S_{i,n+1} - S_{i,n}}{\Delta \tau}. \qquad (46)$$

Rearranging equation (46) gives:

$$\left(1 - \frac{\Delta \tau}{\Delta z} - \alpha \beta \Delta \tau\right) S_{i,n} + \frac{\Delta \tau}{\Delta z} S_{i-1,n} + \beta \Delta \tau e^{-\beta(\tau_n - z_i)} = S_{i,n+1}. \qquad (47)$$

Grid values (solution) can be obtained from equation (47), boundary and initial conditions. The yield was computed by applying the trapezoidal rule at the reactor exit point.

Experimental Methods

Sample Preparation

Hardwood of the hybrid poplar species (Table 1) was obtained frome 1) National Renewable Energy Laboratory, Golden, Colorado. The form of sawdust was screened to the size of 40-100 mesh and used as the feed material. The moisture content was determined to be 8% by measuring the weight differences before and after oven drying for 3 hours at 105°C. Xylan content as xylose equivalent was taken as 21.4 % w/w on the moisture free basis.

Batch Reaction

Reactions were carried out using pyrex glass tubes (11.1 mm ID, 2.4 mm wall thickness, and 200 mm height). One end was sealed and the middle was tapered in a glass shop at Auburn University. First, 0.5 g of dried sample was placed in a tube and 5 g of dilute sulfuric acid solution was added to the tube. The other end was sealed. The wood sawdust and dilute-acid solution were mixed vigorously.

To initiate the reaction, the glass reactor ampules were placed into an oil bath (Haake FS2 model) for which the temperature was preadjusted at 230°C. After 35-50 seconds, depending on reaction temperature, the ampules were transferred into another oil bath pre-set at the desired reaction temperature. The two-oil bath procedure was used to minimize the preheating time. The time when the glass ampule was put into the second oil bath was designated as the zero point of the reaction time. After being subjected to the specified reaction times, the ampules were quenched in an ice-water bath. After enough mixing, one ampule end was broken and the liquid and solid residue were collected for analysis.

Liquid residue analysis procedure

The pH of liquid residues was adjusted to 6-7 with barium hydroxide. The neutralized samples were centrifuged twice at 3000 and 15000 rpm to settle particles. Analysis for xylose was performed by HPLC (Aminex HPX-87P column) (41).

Solid Residue Analysis Procedures

Hot water (7 ml at 85°C) was added to an open ended glass ampule, and the contents were stirred well with a tapered stirrer for washing the solid residue, centrifuged, and poured from the glass ampule. This was repeated until the pH became 5; the glass ampule was put into the oven and was dried completely; 3.6 ml of sulfuric acid (24 N) was added to the opened ended ampule containing the specimen. Using a tapered stirring rod, the specimen was stirred at intervals as required to dissolve the pulp rapidly and completely, leaving the stirring rod in the vial at all times. The tube was placed in a 30°C water bath for one hour. The contents of the centrifuge tube were washed in a 250 ml beaker with 100 ml of water measured in a 100 cc graduated cylinder. The beaker was covered with a watch glass and was placed in an autoclave at 103 Kpa for 1 hr (121°C). The solution was then cooled to room temperature using an ice bath. Bromophenol blue indicator and a magnetic stirring bar were added, and while stirring with a magnetic stirrer, saturated barium hydroxide was added until the solution changed from yellow to blue-violet. The contents of the beaker were then transferred to a 50 cc tapered

Table 1

Chemical Composition of Hybrid Poplar (*Populus eugenell* DN34)

Chemical species	content, % (non-dry basis)	(dry basis)
Moisture	7.00	0.00
Klason Lignin	25.60	27.53
Ash	0.70	0.75
Glucan	48.00	51.61
Xylan	17.20	18.49
Sum	98.50	98.38

centrifuge tube and centrifuged until the supernatant liquid was clear. Most of the solution was decanted into a 300 cc round bottom flask. The clear solution was then boiled under a vacuum created by an aspiratory device the until total volume was reduced between one fifth and one tenth. Analysis for sugars was performed by HPLC(Aminex HPX-87P column).

Results and Discussion

Kinetic Parameter Determination

The kinetics of dilute acid-catalyzed hydrolysis of hybrid poplar hemicellulose was investigated. Figures 2 and 5 show the remaining solid residue vs. time after dilute-acid prehydrolysis of hybrid poplar. The non-linear relationship between residual xylan and time duration clearly indicated that the hemicellulose in hybrid poplar is not a single phase. Yet it appeared that the hemicellulose in this substrate is biphasic. That is, the hemicellulose in hybrid poplar is composed of two different fragments: fast hydrolyzing fraction, denoted by A_F, and slow hydrolyzing fraction, denoted by A_S. This finding was in agreement with the kinetic pattern of hemicellulose hydrolysis in other species of woods, including aspen (49), southern red oak (12) and spruce (13). The reaction pattern was modeled as consecutive reactions of hydrolysis of hemicellulose followed by the decomposition of xylose (51). The kinetic model was therefore set to follow the pattern of parallel-serial reactions. The kinetic parameters (Arrehenius factors and the acid exponents) were experimentally determined by non-linear regression analysis. The results are shown in Table 2. The validity of this kinetic model is seen in the close agreement of the experimental data with the model prediction as shown in Figures 4,5, and 6.

Simulation Program

A computer program based on the theoretical basis described in the previous section was developed to identify the optimum operating conditions of a two-stage percolation type pretreatment reactor. The objective of this computational study was to maximize the yield of sugar (xylose) during pretreatment. The program incorporates experimentally determined kinetic data with the solution of modeling equations. It is composed of one main program and twenty three subroutine programs.

The program was constructed in such a way that it takes in high/low temperatures, acid concentration, residence time, flow rate, and ω(the ratio of velocity in the high temperature phase to the velocity in the low temperature phase) as input data and generates product yield, concentration, and the optimum set of operating conditions as the output. Sample input and output data are given in Table 3.

The computation procedure was as follows. From the input data, the reaction rate constants were calculated. This information was then put into the reactor modeling equation from which the yield and the concentration of product were evaluated. This computation was done with the provision of the additional input parameters of β, ρ and ω. These parameter
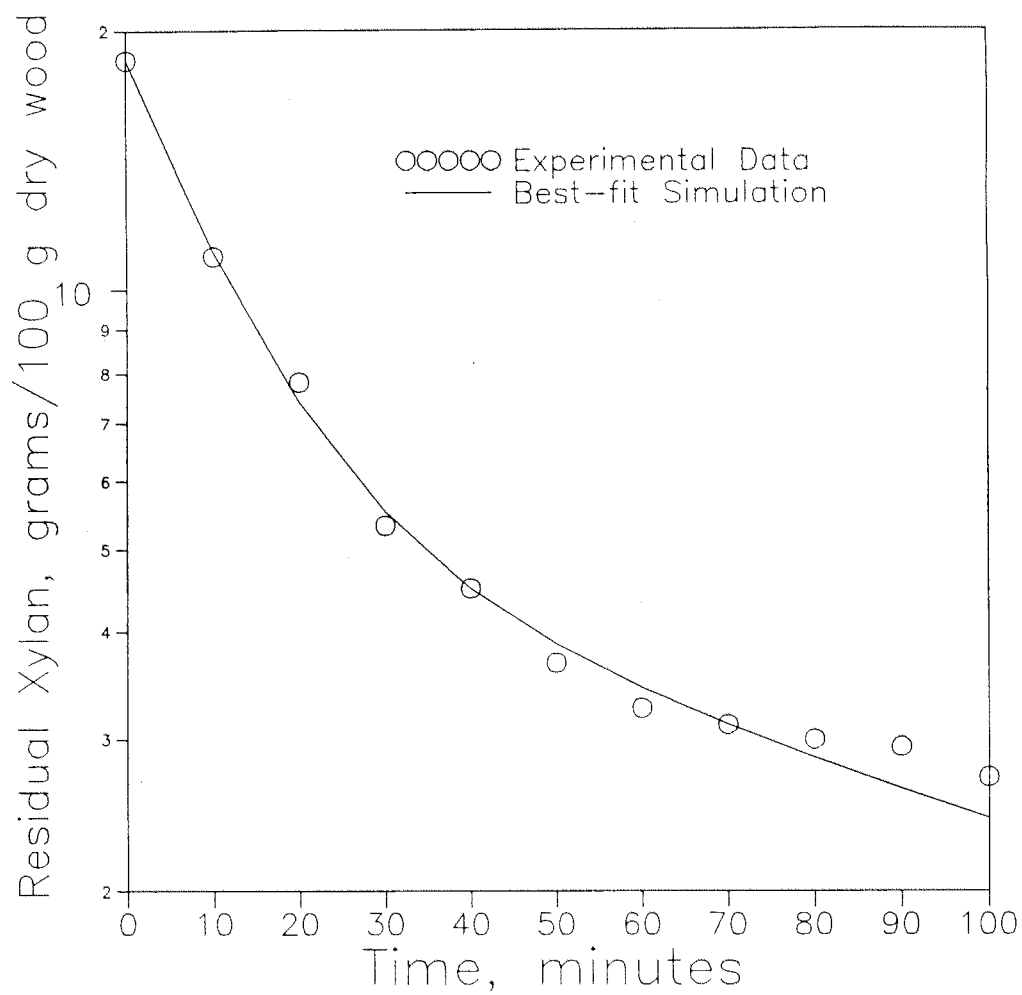
Figure 2.   Residual Xylan vs. the Reaction Time
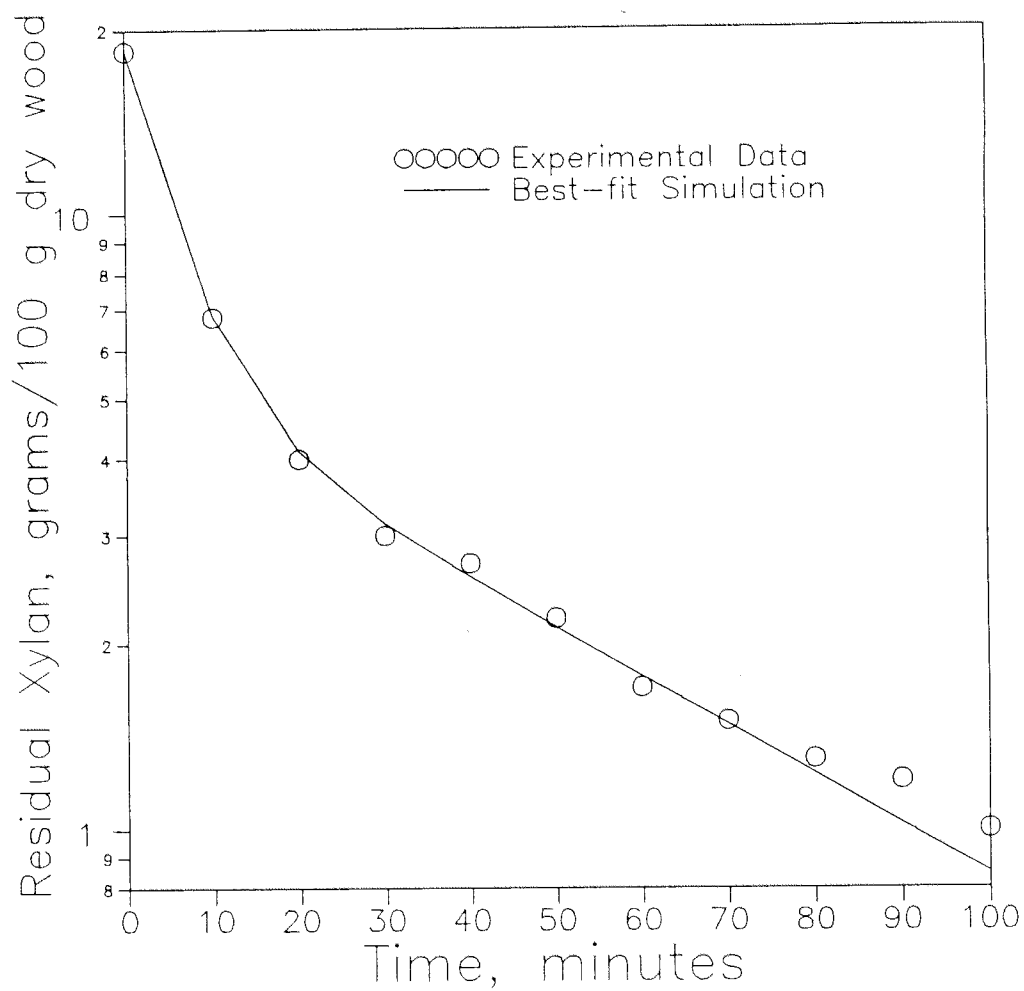
Figure 3.   Residual Xylan vs. the Reaction Time

Table 2

Kinetic Parameters

Reaction No. i	Pre-exponential factor A_i	N_i	Activation energy E_i (cal/g-mole)
1	6.17×10^{13}	1.40	28,000
2	1.88×10^{14}	1.20	31,000
3	1.01×10^{11}	0.48	25,330

Fraction of fast hemicellulose = H_F = 0.71; H_S = 0.29
$k_i = A_i[C]^{N_i} \exp(-E_i/(RT))$
$[C]$ = w/v % of sulfuric acid
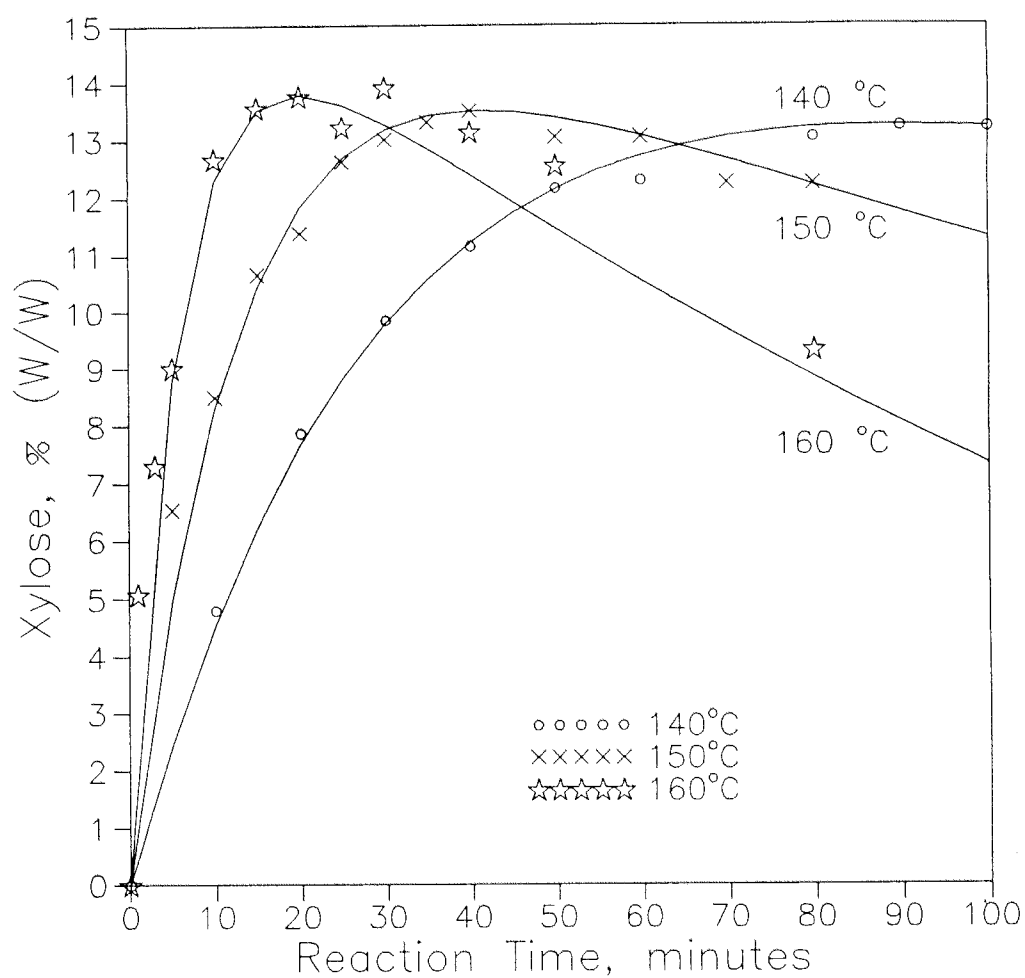
Figure 4.   Reaction Progress in Hydrolysis of Hardwood
             Hemicellulose at 0.49% W/V Sulfuric Acid
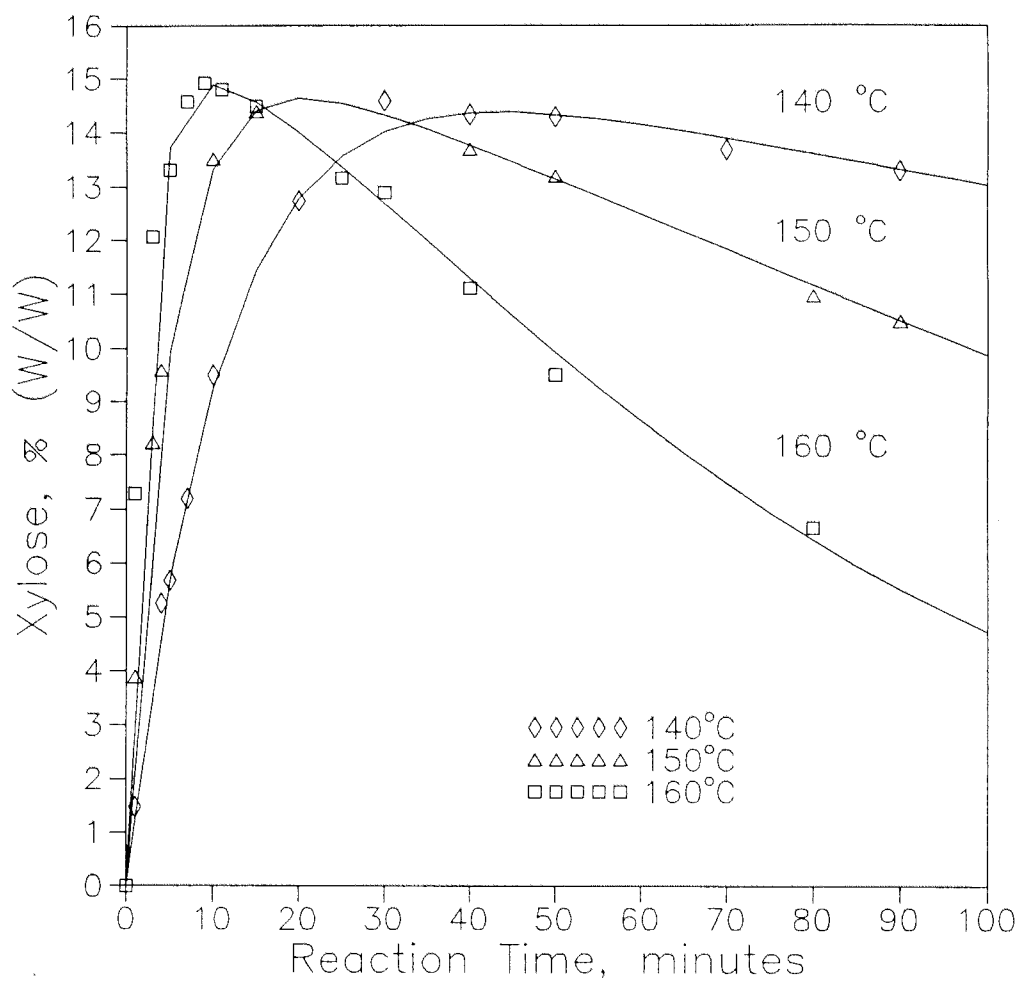
Figure 5.   Reaction Progress in Hydrolysis of Hardwood
              Hemicellulose at 0.98% W/V Sulfuric Acid
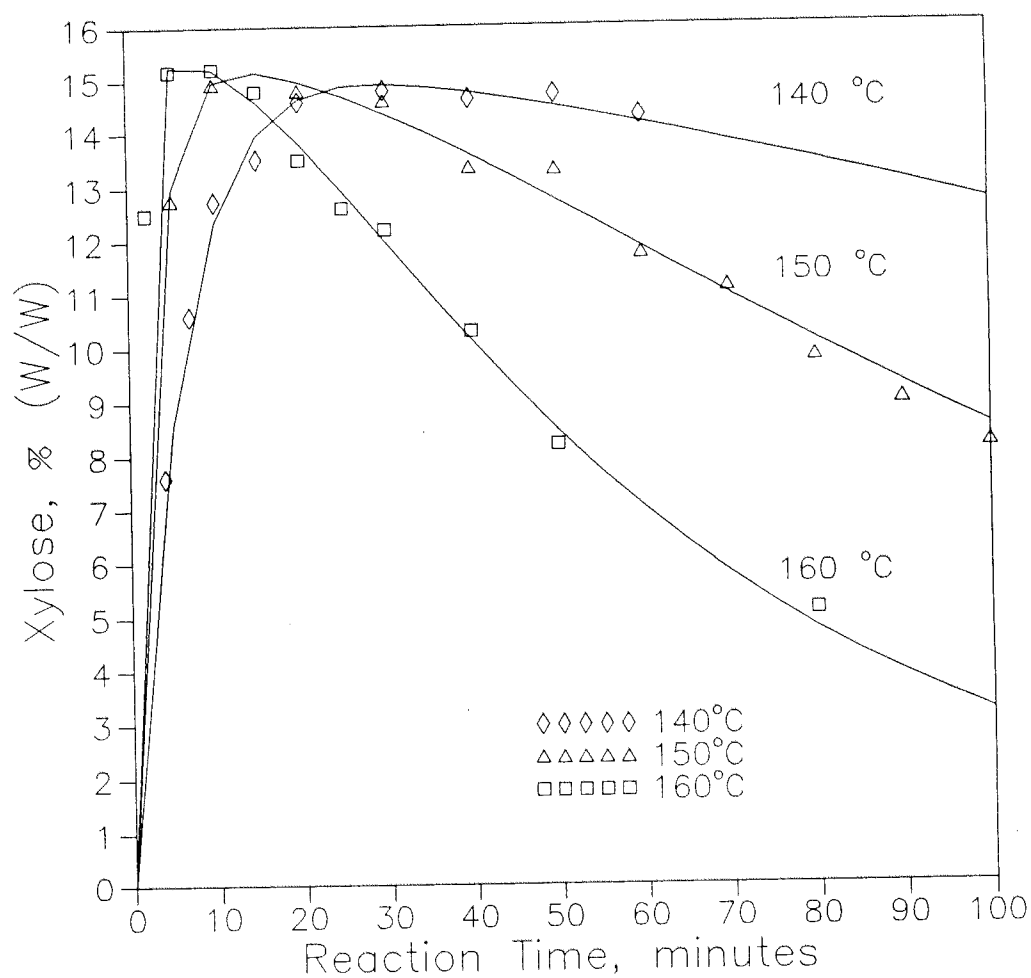
Figure 6.   Reaction Progress in Hydrolysis of Hardwood
            Hemicellulose at 1.47% W/V Sulfuric Acid

Table 3

Sample Output of the Simulation Program

```
                                -----INPUT DATA-----
-----------------------------------------------------------------------------
LOW T(C)     HIGH T(C)     ACID CONC.(%W/V)   LENGTH(CM)  ω=VELOCITY RATIO
-----------------------------------------------------------------------------
    140.0       170.0         0.83370            5.0800            1.7
-----------------------------------------------------------------------------
```

```
                                -----RESULTS-----
   #1 XYLOSE YIELD AND XYLOSE CONCENTRATION UNDER VARIOUS OPERATION MODES
-----------------------------------------------------------------------------
            UNI LOW            UNI HIGH        STEP CHANGE
       TAU   YIELD  CONC.    YIELD  CONC.     YIELD   CONC.
-----------------------------------------------------------------------------
        1   71.26   2.47    75.19   2.61     77.29    2.68
        2   77.31   1.34    81.65   1.42     84.94    1.47
        3   81.07   0.94    85.22   0.99     88.51    1.02
        4   83.68   0.73    87.52   0.76     90.62    0.79
        5   85.58   0.59    89.13   0.62     92.03    0.64
-----------------------------------------------------------------------------
        #2 XYLOSE DECOMPOSED AND HEMICELLULOSE UNREACTED
-----------------------------------------------------------------------------
               UNI LOW            UNI HIGH          STEP CHANGE
     TAU  DECOMP.  HC UNREAC.  DECOMP.  HC UNREAC.  DECOMP. HC UNREAC.
-----------------------------------------------------------------------------
        1    9.67    19.07      10.14   14.67       15.05    7.65
        2    9.86    12.82       9.94    8.41       11.24    3.82
        3    9.90     9.02       8.90    5.88        8.81    2.69
        4    9.55     6.78       8.01    4.47        7.42    1.96
        5    8.85     5.57       7.40    3.47        6.29    1.68
-----------------------------------------------------------------------------
      #3 OPTIMAL REACTION TIME(MINS)& VOLUMETRIC FLOW RATE(CC/MINS)
-----------------------------------------------------------------------------
             UNI LOW        UNI HIGH          STEP CHANGE
   TAU    R.T.    VFR     R.T.    VFR    R.T.1   R.T.2   VFR1    VFR2
-----------------------------------------------------------------------------
    1   70.646  0.303   8.695   2.460  29.345  14.705  0.394   0.669
    2  133.141  0.321  15.760   2.714  33.747  23.304  0.583   0.991
    3  191.561  0.335  20.379   3.148  34.236  27.811  0.787   1.338
    4  239.111  0.358  23.911   3.578  38.801  31.519  0.926   1.574
    5  271.717  0.394  27.172   3.935  38.040  33.565  1.124   1.912
-----------------------------------------------------------------------------
    #4 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM
-----------------------------------------------------------------------------
   TAU      YIELD          CONC            ρ            OPTIMAL β
-----------------------------------------------------------------------------
    1      4.784          74.422         0.540           4.000
    2      2.830          82.918         0.460           2.700
    3      1.948          87.062         0.420           2.000
    4      1.503          89.414         0.420           1.700
    5      1.214          91.058         0.420           1.400
-----------------------------------------------------------------------------
   HC   = Hemicellulose
   R.T. = Reaction time, minutes
   TAU  = τ
   VFR  = Volumetric Flow Rate, cc/minutes
```

values were then optimized to maximize the yield for a given τ value (dimensionless reaction time). The optimization process was done by repeated calculation of the model equation applying multiple levels of each parameters, an exponential design. This computation was done for three different cases of temperature policy: uniformly low temperature, uniformly high temperature, and step-change (from low to high) temperature. Thus, the partial differential equation depicting percolation reactor operation was analytically solved to determine product yield and concentration under various conditions. The simulation was designed to deal with these two factors as affected by reaction temperature, duration of operation (cumulative recovery of product effluent), and optimum flow rate under various reaction conditions.

Non-uniform Temperature (Temperature Step-Change) Policy

The main focus of this study was temperature policy. The conventional temperature strategy in percolation reactor operation has been to apply a uniform temperature throughout. This has previously been reported in a study of simplified kinetics done at Auburn University (3). Because this study of hemicellulose was concerned with biphasic hemicellulose, it was thought that setting the temperature control at a single uniform setting might not be the best solution. For a simple serial reaction, high temperature is preferred because of the activation energy difference between hydrolysis and decomposition. The upper limit of the temperature must be determined by practical considerations. For biphasic substrate, however, applying a uniformly high temperature may cause excessive decomposition of the sugar released from H_F fraction, which builds up at the early phase of the reaction. Whether an optimum uniform temperature exists for a parallel-serial reaction in the percolation reactor is unknown at this time. Consequently, it becomes of interest to see if temperature variation during the process, especially a step-change from uniform low to uniform high, can give better results than either limit. The simulation results addressing this point are summarized in Table 4.

Three sets of temperature ranges were studied: 150 to 180°C, 140 to 170°C, and 165 to 185°C. These temperatures were chosen randomly below 185°C. It is well known that at temperatures above 185°C, an appreciable degree of cellulose hydrolysis occurs, which is highly undesirable in pretreatment practice. The temperature shift (from low to high) was made at about 60% of total reactor operation time. All yields and concentrations were calculated on the basis of a substrate loading of 3.47% weight hemicellulose per volume of liquid. The β value (a quantity inversely proportional to flow rate) was optimized at each reaction temperature and at a given τ value so that it could give maximum xylose yield. The tau τ (dimensionless operation time) was limited to 9 in order to maintain the average product concentration above 0.3% w/v. In all three cases, the xylose yield with step change in temperature was indeed higher than either of the uniform temperature cases. The increase in yield was discernible: about 6.5% over that of the uniform low temperature case, and about 2.5% over that of the uniform high temperature case. A few other noteworthy points were noted from the simulation results. One has to do with the optimum shifting point in the step-change (at what point do we shift the temperature ?). In the numerical exercise, τ was

Table 4

Optimal Yield vs.τ

(Temperature: uniform low, uniform high and step change)

Temperature,°C	τ							
	2	3	4	5	6	7	8	9
150	75.3	79.0	81.7	83.7	85.3	86.5	87.5	88.4
180	79.4	83.1	85.6	87.4	88.7	89.8	90.6	91.3
Step change	81.2	85.5	88.0	89.8	91.0	92.0	92.8	93.4
140	73.8	77.5	80.2	82.2	83.9	85.2	86.3	87.2
170	78.0	81.8	84.4	86.3	87.7	88.8	89.7	90.5
Step change	79.5	84.1	86.8	88.7	90.1	91.1	92.0	92.6
165	77.3	81.1	83.8	85.7	87.1	88.3	89.2	90.0
185	80.0	83.7	86.2	87.9	89.2	90.2	91.0	91.7
Step change	82.7	86.4	88.6	90.2	91.4	92.2	93.0	93.5

Acid Concentration = 0.49 % W/V

fixed at 4, a representative value. The computed yield vs. shifting point is shown in Figure7. For the three cases, the maximum yield occurred with the shifting at 0.55, 0.45 , and 0.6 of total τ for the respective runs.

Rationalization on Yield Improvement in Temperature Step-change Over Uniform temperature

A plausible explanation was also sought as to why the yield with step change is higher than those attainable at low and high end temperatures. It appears that the β value holds the key to this answer. First of all, it was found that there is a vast difference in optimal β value (a quantity inversely proportional to flow rate) between fast hemicellulose and slow hemicellulose. Table 5 lists the β_{opt} values for each hemicellulose fragment. Taking 140 °C as an example, β_{opt} for fast hemicellulose is about one sixth of that for slow hemicellulose. Similar trends are seen at other temperatures. In reference to Table 5, in order to hydrolyze the fast hemicellulose (again at 140°C) in an optimal fashion, one must apply an operating condition such that β_{opt} = 1.15. On the other hand, to do the same for slow hemicellulose one must adjust the β_{opt} to 6.50. Since the slow and fast hemicellulose cannot be processed separately, one must seek a compromised β_{opt}. This β_{opt} was found to be 2.95 (Table 5). Under uniform temperature conditions, the overall β_{opt} lies between the two β_{opt} for each fragment. A similar computation was carried out for the case of step change. Table 6 lists the β_{opt} before and after the temperature shift.

For the step change operation where the temperature shifts from 165°C to 185°C, the β_{opt} shifts accordingly from 1.92 to 7.82. The shift of β in this case can be practiced in reactor operation simply by adjusting the inlet fluid temperature and the flow rate. It is to be noted that the initial β_{opt} of 1.92 is close to 1.19, the optimal value for fast hemicellulose at 165°C. The final β_{opt} of 7.82 is somewhat close to 5.69, the β_{opt} for slow hemicellulose computed at 185°C. With the step change in effect, at the low temperature phase (early phase) the reaction and operating condition is set to work primarily on the fast hemicellulose fraction. At the shifting point, the substrate contains mostly the slow hemicellulose. At the high temperature phase (latter phase) reaction and operating condition is readjusted to work primarily on the slow hemicellulose. It is believed that the reason for the projected yield improvement is associated with the step change of temperature during the percolation reactor operation.

Optimal temperature difference

The previous sections show that the yields with stepchange temperature policy in the three sample cases are higher than those with uniform high or uniform low temperature operation. In this work the temperature policy was further refined. The first item investigated in this regard was to determine the optimum level of temperature difference in step change operation. Figure 8 shows the sugar yield vs temperature difference when low temperature is 140, 150, and 160°C. Highest yield occurred when the temperature difference was 28, 29 and 29°C respectively. It appears that with representative reactor operating
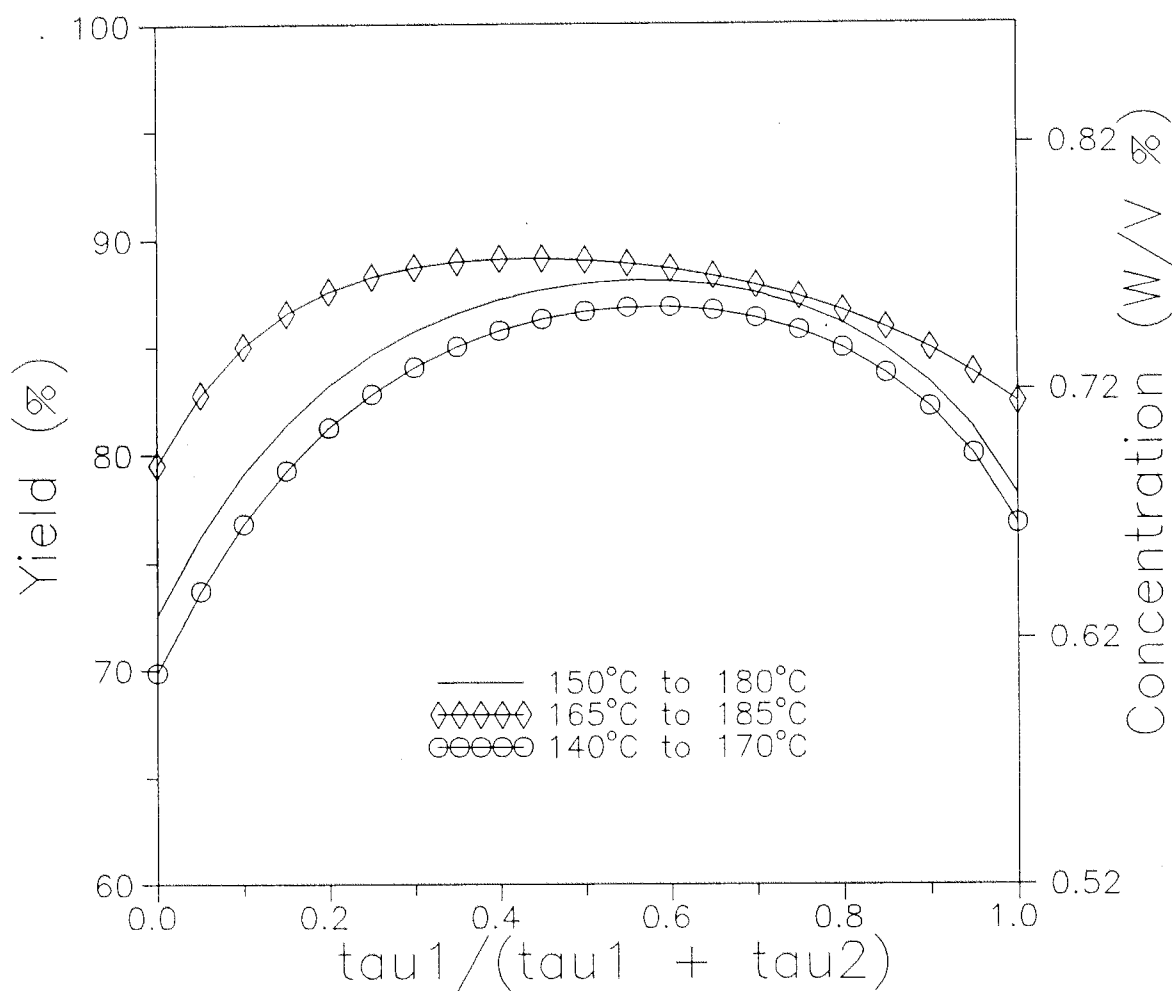
Figure 7.   Yield(Concentration) vs. $\tau 1/(\tau 1 + \tau 2)$

Table 5

β_{opt} Values for A_F, A_S, and for Combined Hemicellulose

Temperature		β_{opt}	for
°C	A_F	A_S	$A_F + A_S$
140	1.15	6.50	2.95
150	1.17	6.32	3.07
165	1.19	6.04	3.19
170	1.20	5.95	3.21
180	1.22	5.77	3.24
185	1.23	5.69	3.25

Table 6

β_{opt} for Step-Change of Temperature

1st Temp.	2nd Temp.	Before step change	After step change
°C	°C	(value of A_F)	(value of A_S)
150	180	1.21 (1.17)	10.97 (5.77)
140	170	1.15 (1.15)	11.57 (5.95)
165	185	1.92 (1.19)	7.82 (5.69)
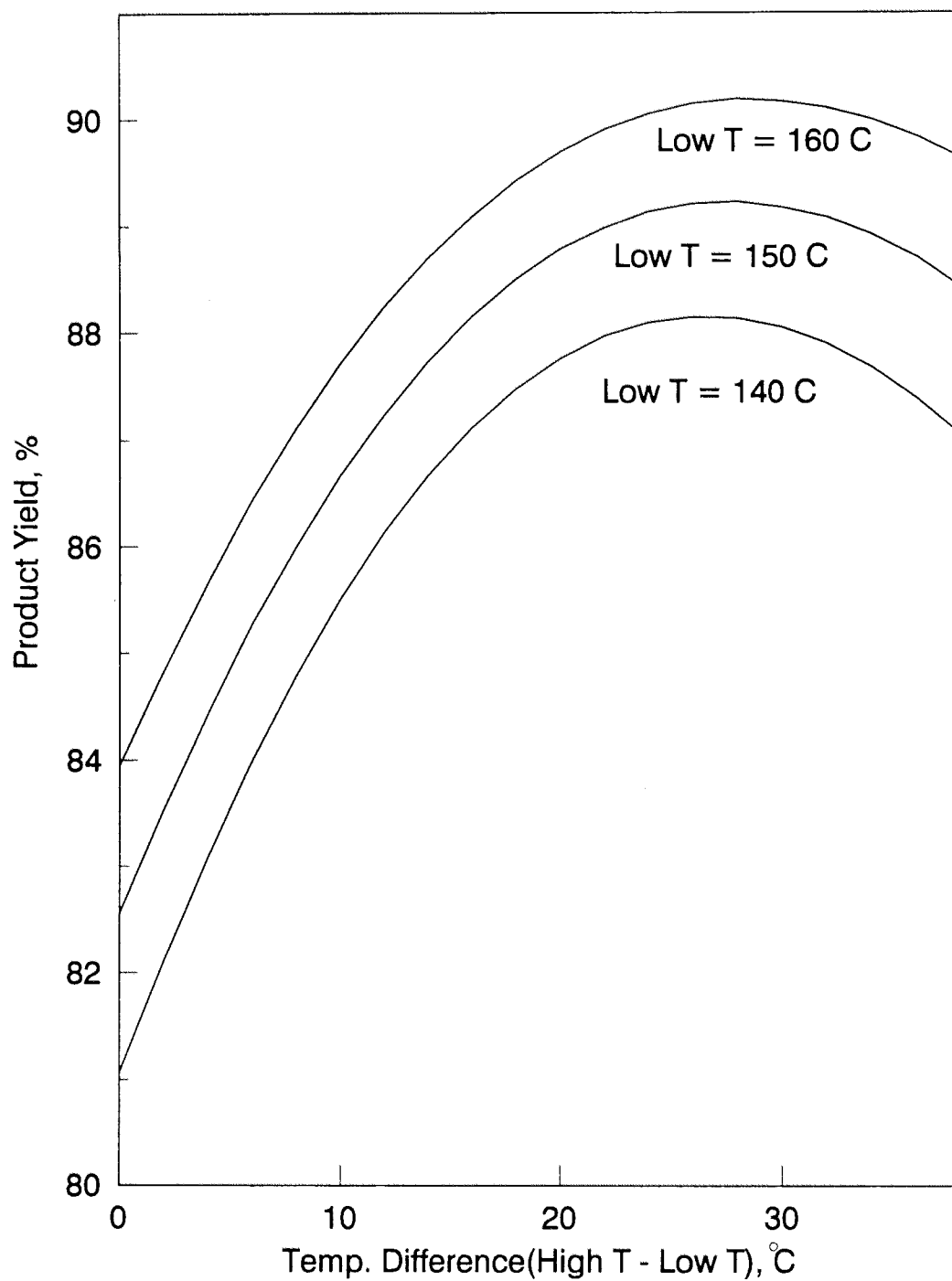
$(\mathrm{T}=3.0, [H_2SO_4] = 0.17 \text{ N})$

Figure 8.   Effect of Temperature Difference on Product
            Yield in Step-change Operation

conditions: acid concentration = 0.83 % w/v (0.17 N sulfuric acid) and tau=3, the optimal temperature difference is about 30°C. For example, when low temp is set at 150°C, the optimum high temperature should be 180°C. The reactor is then first run at 150°C for a certain duration, then at 180°C for the remainder of the operation.

Step-change of Flow Rate (along with temperature)

The preceding simulation was conducted with the assumption that the liquid flow rate is kept uniform throughout the reactor operation for a given run, even though the temperature has gone through a step change. The simulation process was refined by eliminating this assumption. From the previous simulation results, it became obvious that the β value ($k_L L/u$) has a profound effect on the xylose yield. Since β is an operational parameter involving both the reaction temperature and the flow rate, it is probable that the β value shift, due to change of velocity (along with temperature), may also affect the xylose yield. In an effort to verify this, the velocity ratio was included between the two phases of reactor operation as an additional adjustable parameter in the percolation reactor simulator program. The ratio of velocity in high temperature phase to the velocity in low temperature phase was defined as ω. The simulator program was run for ω = 0.5, 1.0, 1.5, 2.0, and 2.5, covering two different temperature ranges. The results are listed in Table 7. The column for ω = 1.0 in the table represents the base case (uniform velocity). Taking 140-170°C, and τ = 2.0 as an example, the highest yield of 84.92 % occurred at ω = 2.0. The improvement (ω=2.0) over the base case (84.32 %) is then 0.6 %. The average value of yield improvement for various cases listed in Table 7 is estimated to be about 0.5 %. The effect of ω on product yield is also shown in Fig. 9. In this figure, the maximum yield is seen to occur at ω value slightly less than 2. In view of the fact that the velocity variation is a simple operational adjustment, it would be a worthy item to be considered in process design and operation.

Two-stage Reverse-flow Percolation Reactor

The yield increases consistently with τ, whereas the product concentration is expected to decrease with it. An inverse relationship thus exists between the yield and the product concentration. A point to emphasize is that the sugar concentration of the product is an important factor in the economics and energy efficiency of overall biomass processing. Obviously the higher the concentration, the less processing cost and energy would be required in the final product separation phase such as distillation of fermentation products. Certainly there is a trade-off between the yield and product concentration. The true optimum point can only be determined from consideration of the overall process economics.

In this regard an intriguing idea was developed by NREL investigators and made available for the author to analyze from a theoretical standpoint. This concept also involves two-stage processing of biomass as was done in the preceding simulation study. However, there is an important modification in the process. The biomass is first treated at a low

3 3

Table 7

Effect of Velocity Step-Change on Xylose Yield

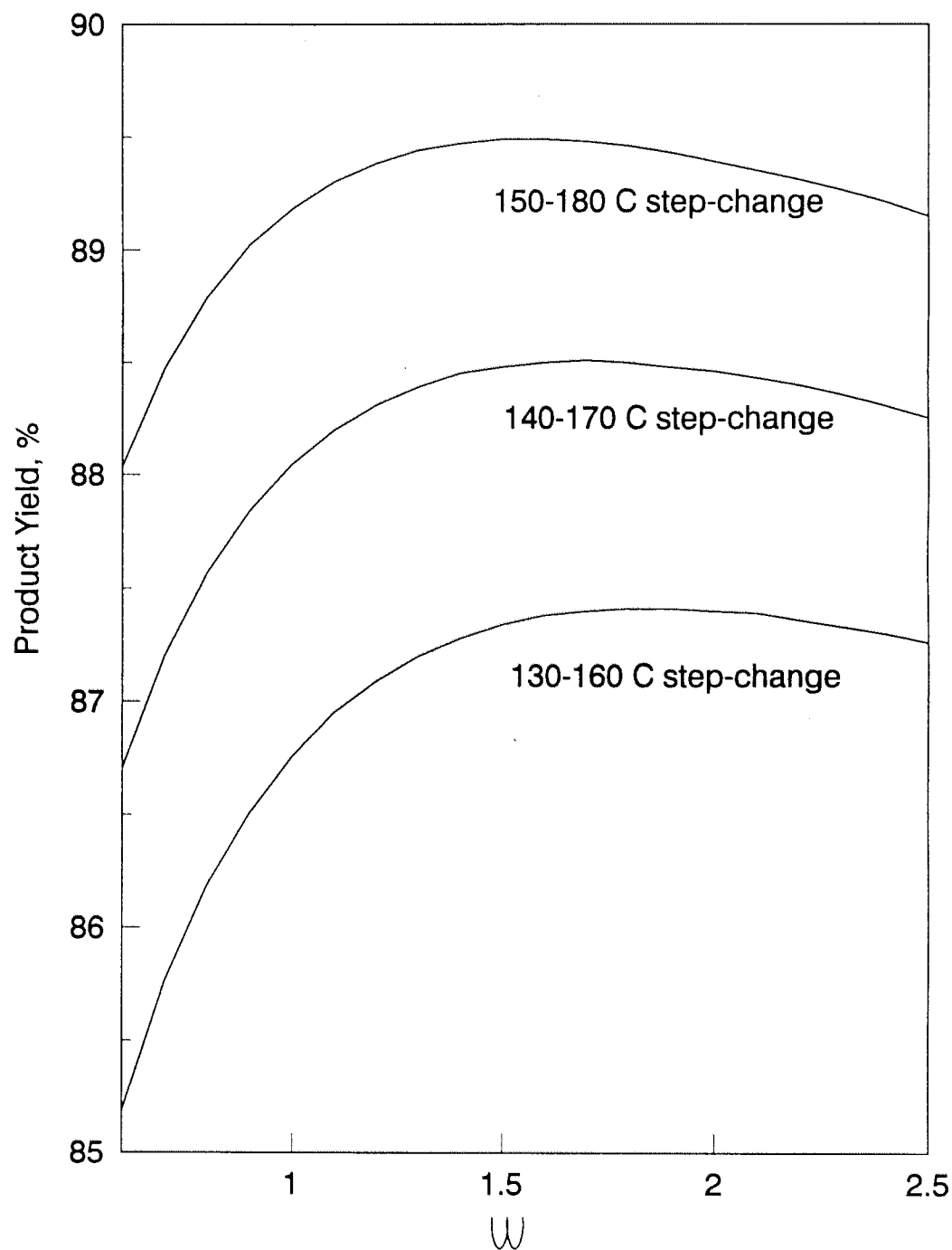|	Yield									
T set	140 - 170°C					150 - 180°C				
τ ω = 0.5,	1.0,	1.5,	2.0,	2.5,	0.5,	1.0,	1.5,	2.0,	2.5,	
1 74.26	76.40	77.17	77.36	77.27	75.95	78.09	78.74	78.81	78.65	
2 82.01	84.32	84.89	84.92	84.73	83.61	85.69	86.12	86.05	85.80	
3 86.01	88.05	88.48	88.46	88.26	87.42	89.18	89.49	89.39	89.15	
4 88.50	90.27	90.61	90.57	90.37	89.74	91.23	91.46	91.36	91.13	
5 90.21	91.75	92.03	91.97	91.79	91.30	92.59	92.77	92.67	92.46	

($[H_2SO_4]$ = 0.17 N)

Figure 9.   Effect of Flow-rate ratio on Product Yield

$([H_2SO_4] = 0.17 \text{ N}, \mathcal{T} = 3.0)$

temperature in the percolation mode. Then it is treated again at a high temperature. Up to this point the procedure is identical to the preceding two-stages process with a step-change in temperature. The throughput stream from the high temperature treatment is again put through a percolation reactor packed with fresh biomass at low temperature. The residue in this reactor is then treated with fresh acid at high temperature. This process is repeated. Figure 10 illustrates the difference between temperature step-change and two-stage reverse flow configuration.

Depending upon the acid throughput applied at each stage of the processing, the process stream for low temperature processing is either supplemented with fresh acid or partially bypassed to the sugar product as shown in Figure 11. The term ρ in Figure 13 is defined as the amount of the liquid used at high temperature processing over the total amount of liquid used for the entire process. Because the reverse flow is operated based on temperature step-change, the ρ value which is pre-determined in the temperature step change is also used in reverse flow arrangement. The ρ value of 0.5 thus indicates that the amount of liquid throughput in the reactor for high temperature processing is the same as that for low temperature processing. The overall contact pattern in this process resembles that of a counter-current reactor in that fresh biomass is met with the acid effluent containing the sugar product, and the fresh acid is met with the partially-treated biomass. This process thus combines the concept of two-stage processing and a counter-current processing. Counter-current processing is effective in attaining a high product concentration as evidenced in the leaching processes. In the percolation process, the product yield is inversely related to product concentration. From this viewpoint, the reverse-flow reactor concept should apply well, especially for the percolation reactor system.

The results of the simulation with optimized process parameters are summarized in Table 8 and in Figure 12. Since yield is inversely related with τ, and thus with product concentration, the yield value alone is rather meaningless in the percolation process. To make a valid comparison, the yield value must be taken at a given level of product concentration. Taking an example from Table 8, for the case of the 140-170 °C step-change percolation reactor operation without reverse-flow arrangement, the yield and concentration of xylose at $\tau = 2$ is 84.94 % and 1.47 % w/v, respectively. Looking at the next column, under the same reaction conditions but with a reverse-flow arrangement, at $\tau = 4$, the xylose yield is 89.41%, and the xylose concentration is 1.50 % w/v. Comparing the two cases (with and without reverse-flow arrangement), a significant improvement of yield was found from 84.94% to 89.41% at the same product concentration level (1.47-1.50%). The superior performance of the reverse-flow reactor is also shown in Figure 14, where the yield vs. concentration curve for this reactor is positioned above all other cases of percolation reactor operations. It is believed that the result of this simulation is a positive indication that the proposed reverse-flow reactor scheme is superior to any other known reactor arrangement, especially in attaining high yield and/or product concentration. The main reason for the existence of variational optimal temperature is the biphasic nature of the hemicellulose in the biomass.

TWO-STAGE STEP-CHANGE

Product Stream

Reactor1 (High T)

Reactor2 (Low T)

TREATED BIOMASS
AT LOW T

FRESH BIOMASS

Fresh Acid   Fresh Acid

TWO-STAGE REVERSE-FLOW

Product Stream

Reactor1 (High T)

Reactor2 (Low T)

TREATED BIOMASS
AT LOW T

FRESH BIOMASS

Fresh Acid
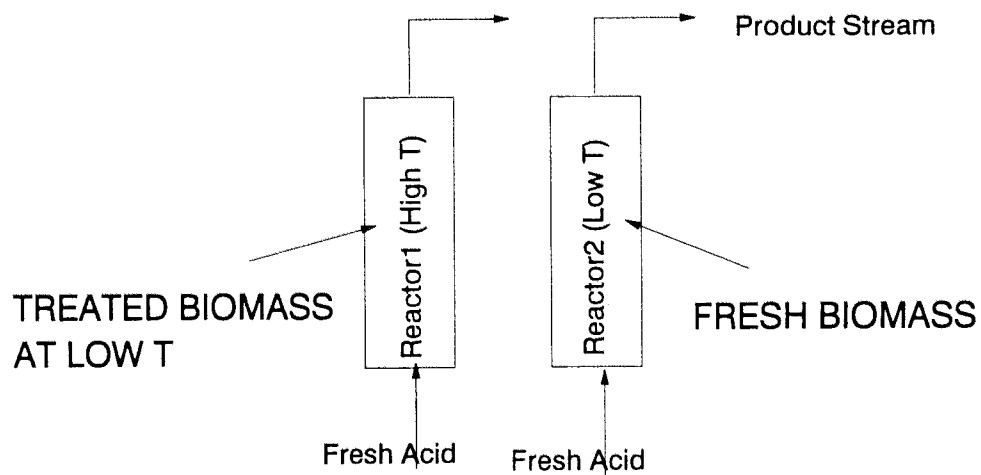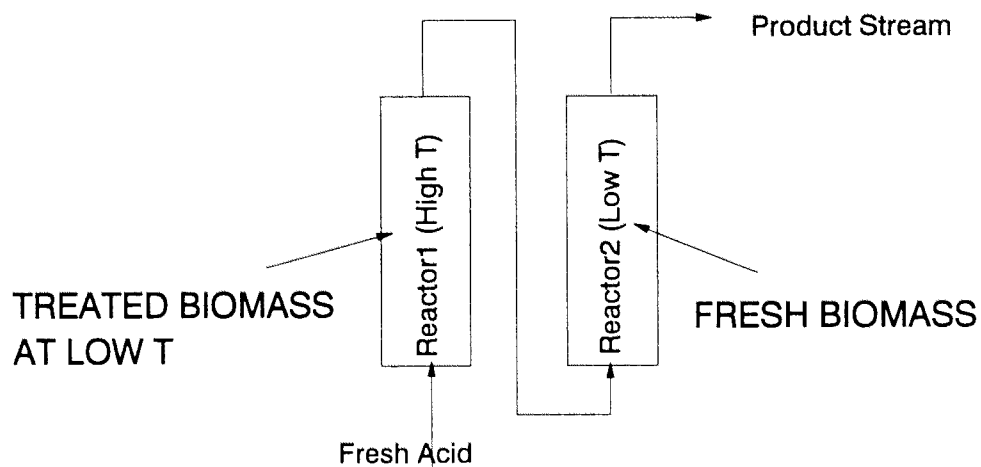
Figure 10.   Schematics of Temperature Step-change and
Two-stage Reverse Flow
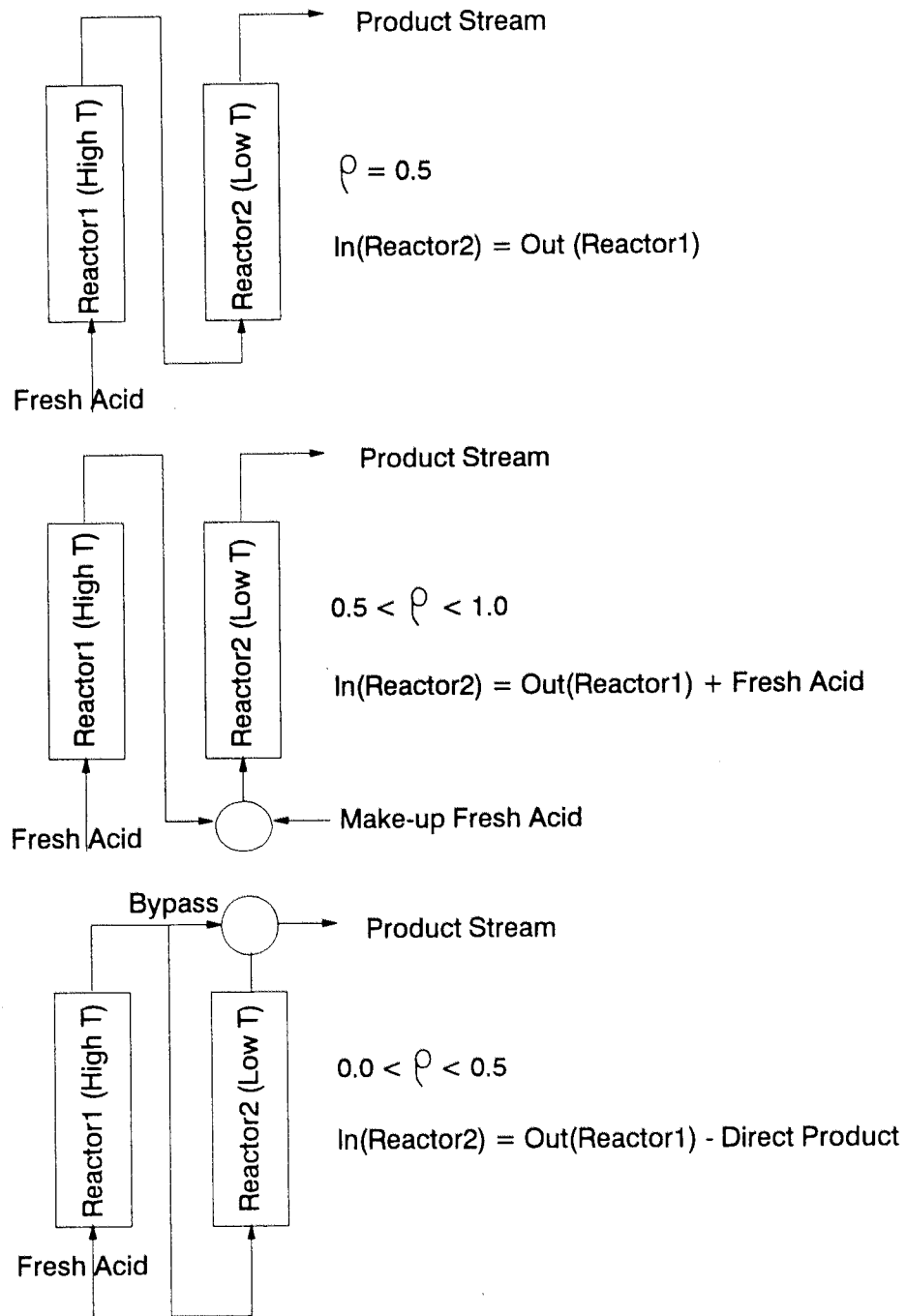
Figure 11. Flow Configuration in Reverse-Flow Two-stage Percolation reactor

Table 8

Xylose Yield and Concentration
in Two-Stage Reverse-Flow Percolation Reactor

τ	140-170°C (ω=1.7)				150-180°C (ω=1.6)			
	w/o R-flow		w/ R-flow		w/o R-flow		w/ R-flow	
	Yld	Conc.	Yld	Conc.	Yld	Conc.	Yld	Conc.
1	77.29	2.68	74.42	4.78	78.78	2.73	75.85	5.06
2	84.94	1.47	82.92	2.83	86.13	1.49	84.20	2.87
3	88.51	1.02	87.06	1.95	89.49	1.04	88.11	1.97
4	90.62	0.79	89.41	1.50	91.46	0.79	90.38	1.51
5	92.03	0.64	91.06	1.21	92.76	0.64	91.90	1.22

$[H_2SO_4]$ = 0.17 N
R-flow: reverse-flow
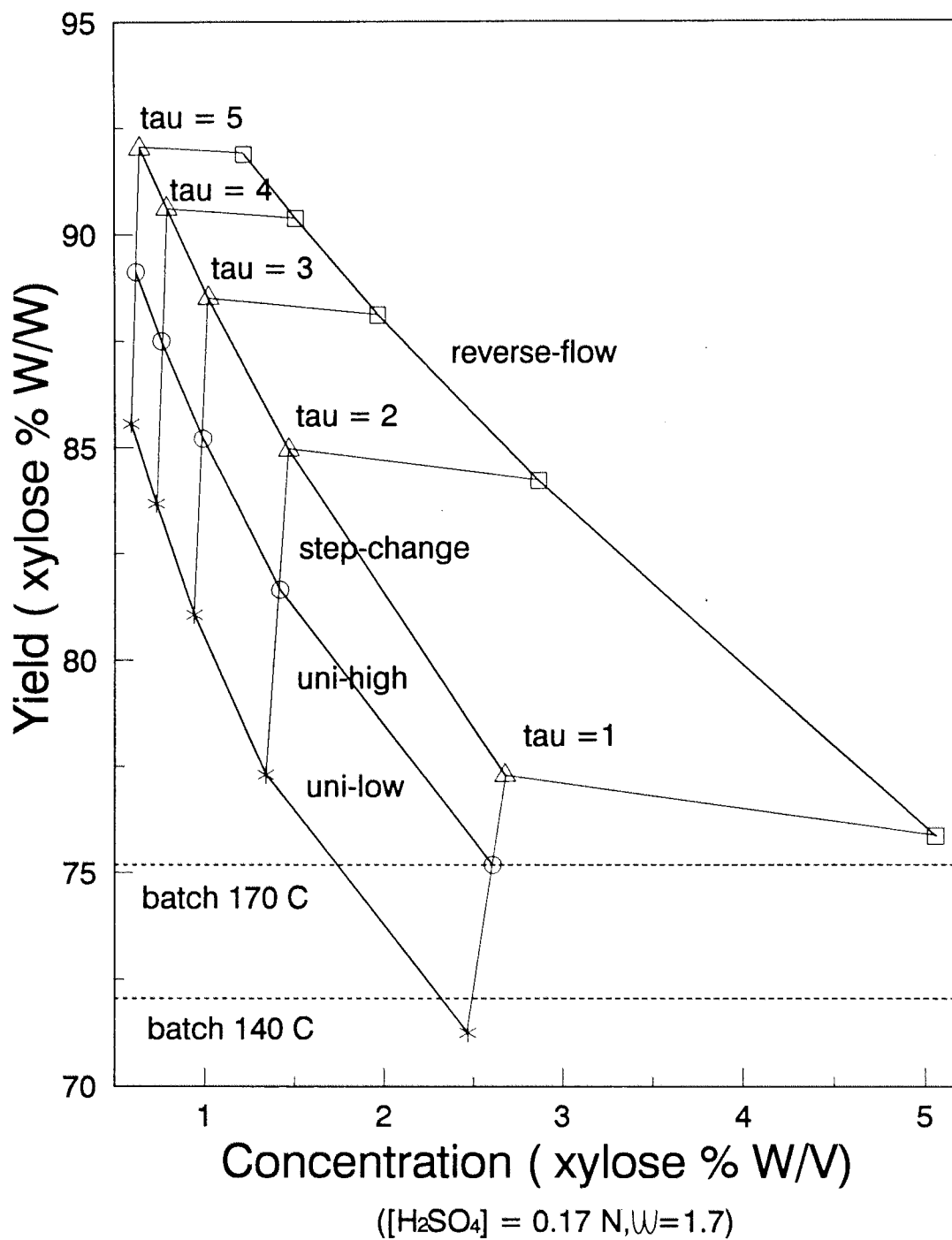
Figure 12.   Yield vs. Product Concentration Under Various Operation
Modes of Percolation Reactor

Effect of intraparticle sugar diffusion on yield

Intraparticle diffusion of the sugar component is a factor adversely affecting the performance of a percolation reactor. The effect of intraparticle sugar diffusion is related to product yield, and size reduction of biomass feed. The analytical results in the diffusion model were used as a component in the reactor simulation program. Two cases of temperature policy (140-170°C and 150-180°C) were chosen and studied for the effect of the intraparticle diffusion of xylose on product yield. The computational results concerning the effect of intraparticle diffusion are summarized in Figures 13 and 14. Each figure consists of two parts: Yield vs. Thiele Modulus and Chip Thickness vs. Thiele Modulus. These figures are constructed in such a way that one can determine the yield in relation to chip-size and reaction condition. For example, in Figure 13, when chip thickness = 0.29 cm, Thiele Modulus is 0.5 (from lower figure) and the corresponding product yield is 79.2% (from upper figure).

The characteristic length (particle size) was determined as follows: taking the example of 150 -180°C step-change, it is seen from Figure 13 that for ϕ (Thiele Modulus) < 0.5, the intraparticle diffusion becomes insignificant. To put this in practical terms, the following values of estimated parameters were used (52-55): D_e (effective diffusivity) = D x (microporosity) = 0.0000565 x 0.52 = 2.94 x 10^{-5} cm^2/sec, and k_3 (xylose decomposition rate at 165°C = average value of 150 and 180°C, 0.17 N H_2SO_4) = 0.000357 sec^{-1}.

$$\phi(\textit{thiele modulus}) - b(\frac{k_3}{D_e})^{0.5} \qquad (48)$$

Substituting these values into ϕ < 0.5 one obtains, b (characteristic length = half of thickness) < 0.145 cm (from Eqn.(14)). For woody material, it is known that the diffusion occurs mostly in the longitudinal direction. Therefore, the effect of intraparticle diffusion is insignificant if the size of feed material (in the longitudinal direction) is less than 0.29 cm. Conversely, for the particle size greater than this the intraparticle diffusion becomes progressively more important. Therefore, the critical chip thickness is 0.29 cm for 150-180°C step-change operation. Similarly, the critical chip thickness for 140-170°C was determined to be 0.4 cm.

Applicability of the Modeling Investigation to Southern Red Oak and Aspen.

Since hemicellulose in most hardwood species is known to be composed of two different segments (fast hydrolyzing fraction and the slow hydrolyzing fraction), it is of interest to see whether these findings are applicable to other hardwood species. For this purpose, southern red oak and aspen were selected and subjected for modeling investigation. The kinetic parameters of southern red oak and aspen are shown in Table 9. The percolation reactor simulation was performed on the basis of these kinetic data. Table
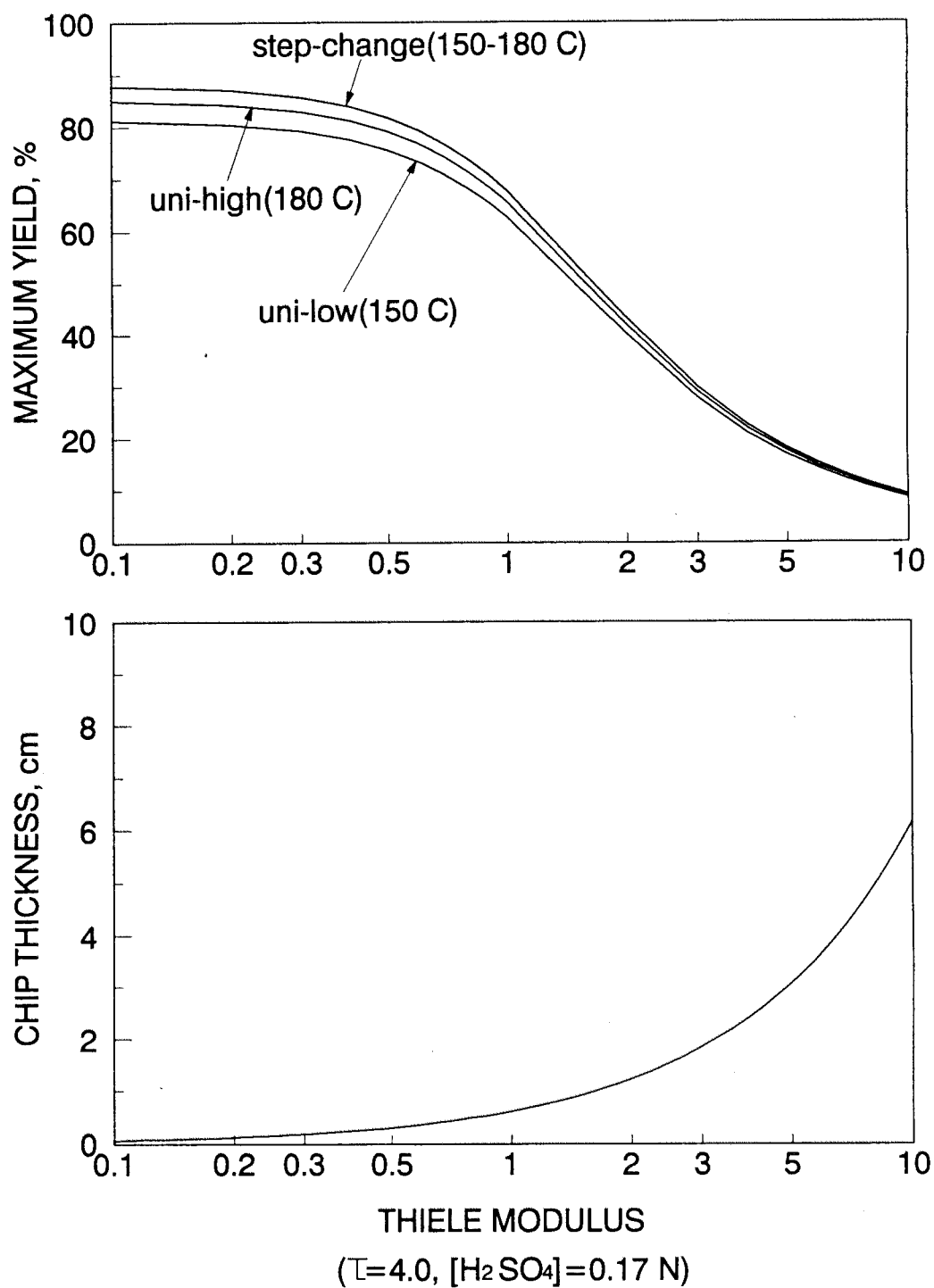
Figure 13.   Effect of Intraparticle Diffusion on Product Yield:
Yield vs. Chip-thickness
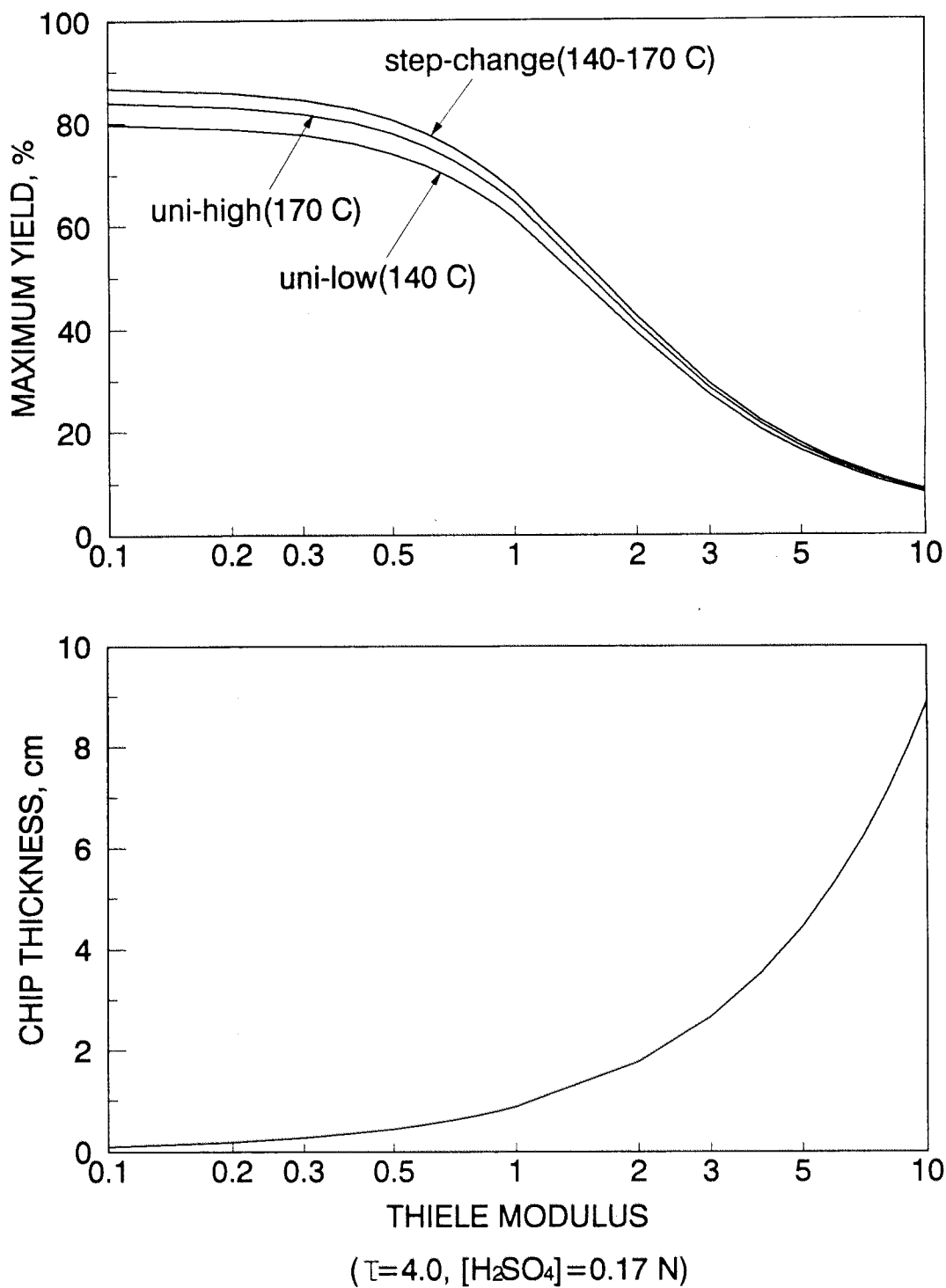
Figure 14. Effect of Intraparticle Diffusion on Product Yield:
Yield vs. Chip-Thickness

Table 9

Kinetic parameters of hemicellulose hydrolysis

---

southern red oak (12)

---

fast hemicellulose fraction	0.7

$$k1(\text{ fast fraction to xylose}) = 1.036 \times 10^{14} \times (\text{acid})^{1.54} \times e^{(-28680/RT)}$$

slow hemicellulose fraction	0.3

$$k2(\text{ slow fraction to xylose}) = 5.995 \times 10^{12} \times (\text{acid})^{1.19} \times e^{(-28200/RT)}$$

---

aspen (11)

---

fast hemicellulose fraction	0.76

$$k1(\text{ fast fraction to xylose}) = 7.31 \times 10^{17} \times (\text{acid})^{1.00} \times e^{(-37000/RT)}$$

slow hemicellulose fraction	0.24

$$k2(\text{ slow fraction to xylose}) = 1.29 \times 10^{14} \times (\text{acid})^{1.00} \times e^{(-26900/RT)}$$

---

hybrid poplar (14)

---

fast hemicellulose fraction	0.71

$$k1(\text{ fast fraction to xylose}) = 6.17 \times 10^{13} \times (\text{acid})^{1.40} \times e^{(-28000/RT)}$$

slow hemicellulose fraction	0.29

$$k2(\text{ slow fraction to xylose}) = 1.88 \times 10^{14} \times (\text{acid})^{1.20} \times e^{(-31000/RT)}$$

---

10 and Table 11 list the percolation reactor simulation results for southern red oak and aspen, respectively. Again the xylose yield and concentration under various operation modes of percolation were computed. Figure 15 shows the yield vs. concentration in the dilute-acid pretreatment of southern red oak. As was the case with the hybrid poplar, the yield of temperature step-change is 3% higher than that of uniform high and 5% higher than that of uniform low temperature. Also, the reverse flow scheme gave 2.5% yield improvement. The same type of plot was constructed (Fig. 16). The yield improvement for aspen for the case of temperature step-change was slightly lower than that of southern red oak; 1% higher than that of uniform high temperature, and 3% higher than that of uniform-low temperature. The reverse-flow gave an additional 2% yield improvement. In both species the yield in temperature step-change is higher than that of either limit uniform temperature, and the additional yield improvement was obtained with the reverse flow arrangement. The results are in agreement with those of hybrid poplar.

Modification of Kinetics to Account for Presence of Xylo-oligomer

Since soluble xylo-oligomer is formed from xylan and is further hydrolyzed to xylose, xylo-oligomer was added to the base model as one of the recognizable components. As shown in the Oligomer Model section, material balances on xylo-oligomer and xylose for a percolation reactor were set up and simplified as partial differential equations. The partial differential equations were again solved by the Laplace transform method. The solution provides the information for the time-and-position dependent concentrations for the respective components. Upon integration of the concentration over a specified time period, one obtains the yield information for xylose and xylo-oligomer.

The kinetic information (xylo-oligomer to xylose decomposition rate, k_4) available from the literature was put into the revised model to test its applicability. Since the reported data cover temperatures only up to 120°C, they were extrapolated to the current operating conditions of 140-170°C. The simulation results based on this extrapolation to our current operation conditions were quite close to zero. Since it was experimentally proven in recent NREL investigation that the amount of xylo-oligomer as the product in a percolation reactor is indeed discernable, it was concluded that extrapolation of the kinetic data in this case is inappropriate, perhaps due to excessive range of extrapolation.

In order to verify the effect of kinetic parameters on the performance of the percolation reactor, a wide range of presumed γ value (the ratio of the rate from xylan to xylo-oligomer to that for xylo-oligomer to xylose) instead of the γ value from the literature was used in this model. The γ value ranging from 1 to 100 were put into the simulation program and the total yield (the sum of xylose and xylo-oligomer) was calculated. Figure 17 shows total yields vs. τ in uniform temperature under various γ values. The same type of plot with temperature step-change is given in Fig. 18. In both cases, as expected, the yield was seen to be inversely related to the γ value at the fixed τ. At upper limit value, $\gamma = 100$, since xylo-oligomer decomposes as soon as it forms, the yield was the same as that without oligomer inclusion. However, at the other limit value of $\gamma = 1.0$, the increase in yield was

Table 10

Output of the Simulation Program (southern red oak)

```
                            -----INPUT DATA-----
-------------------------------------------------------------------------
LOW T(C)     HIGH T(C)      ACID CONC.(%W/V)   LENGTH(CM)  W=VELOCITY RATIO
-------------------------------------------------------------------------
  140.0       170.0           0.83370            5.0800          1.0
-------------------------------------------------------------------------
                             -----RESULTS-----
        #1 XYLOSE YIELD(%), DECOMPOSED(%)& HEMICELLULOSE UNREACTED(%)
-------------------------------------------------------------------------
             UNI LOW            UNI HIGH            STEP CHANGE
     TAU  YIELD DECOMP HC    YIELD DECOMP HC     YIELD  CONC. DECOMP HC
-------------------------------------------------------------------------
     1   80.52  4.08 15.40  84.53  7.98 7.49   87.87  3.05  11.15  0.98
     2   87.83  4.45  7.73  89.99  6.90 3.11   92.80  1.61   6.88  0.32
     3   91.45  4.63  3.92  92.39  5.46 2.15   94.77  1.10   4.99  0.24
     4   93.29  4.73  1.99  93.79  4.66 1.55   95.86  0.83   3.98  0.15
     5   94.29  4.29  1.42  94.72  3.96 1.32   96.57  0.67   3.30  0.13
-------------------------------------------------------------------------


     #2 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM
-------------------------------------------------------------------------
     TAU    PRODUCT CONC.   PRODUCT YIELD   RHO        OPTIMAL BETA
-------------------------------------------------------------------------
      1        5.363          86.531       0.560          4.300
      2        2.849          91.941       0.560          3.000
      3        2.017          94.124       0.540          2.100
      4        1.591          95.332       0.520          1.700
      5        1.283          96.125       0.520          1.400
-------------------------------------------------------------------------
```

Table 11

Output of the Simulation Program (aspen)

```
                          -----INPUT DATA-----
-----------------------------------------------------------------------
LOW T(C)    HIGH T(C)     ACID CONC.(%W/V)    LENGTH(CM)   W=VELOCITY RATIO
-----------------------------------------------------------------------
   120.0       130.0            1.0             5.0800            1.0
-----------------------------------------------------------------------
                          -----RESULTS-----
        #1 XYLOSE YIELD(%), DECOMPOSED(%)& HEMICELLULOSE UNREACTED(%)
-----------------------------------------------------------------------
                UNI LOW              UNI HIGH              STEP CHANGE
  TAU   YIELD DECOMP HC     YIELD  DECOMP HC     YIELD   CONC. DECOMP HC

   1    83.21 12.17  4.62   86.51   10.10  3.40   87.64   3.04  10.21  2.15
   2    89.65  7.82  2.54   91.84    6.38  1.78   92.66   1.61   6.46  0.89
   3    92.34  6.12  1.54   94.01    4.70  1.29   94.69   1.10   4.69  0.62
   4    93.85  4.76  1.39   95.22    3.85  0.93   95.81   0.83   3.74  0.45
   5    94.83  4.32  0.84   96.00    3.19  0.82   96.53   0.67   3.10  0.37
-----------------------------------------------------------------------


    #2 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM
-----------------------------------------------------------------------
   TAU    PRODUCT CONC.   PRODUCT YIELD   RHO         OPTIMAL BETA
-----------------------------------------------------------------------
    1         4.765          86.063       0.220          1.200
    2         2.713          91.366       0.280          0.800
    3         1.927          93.624       0.320          0.600
    4         1.516          94.874       0.360          0.500
    5         1.192          95.834       0.320          0.400
-----------------------------------------------------------------------
```
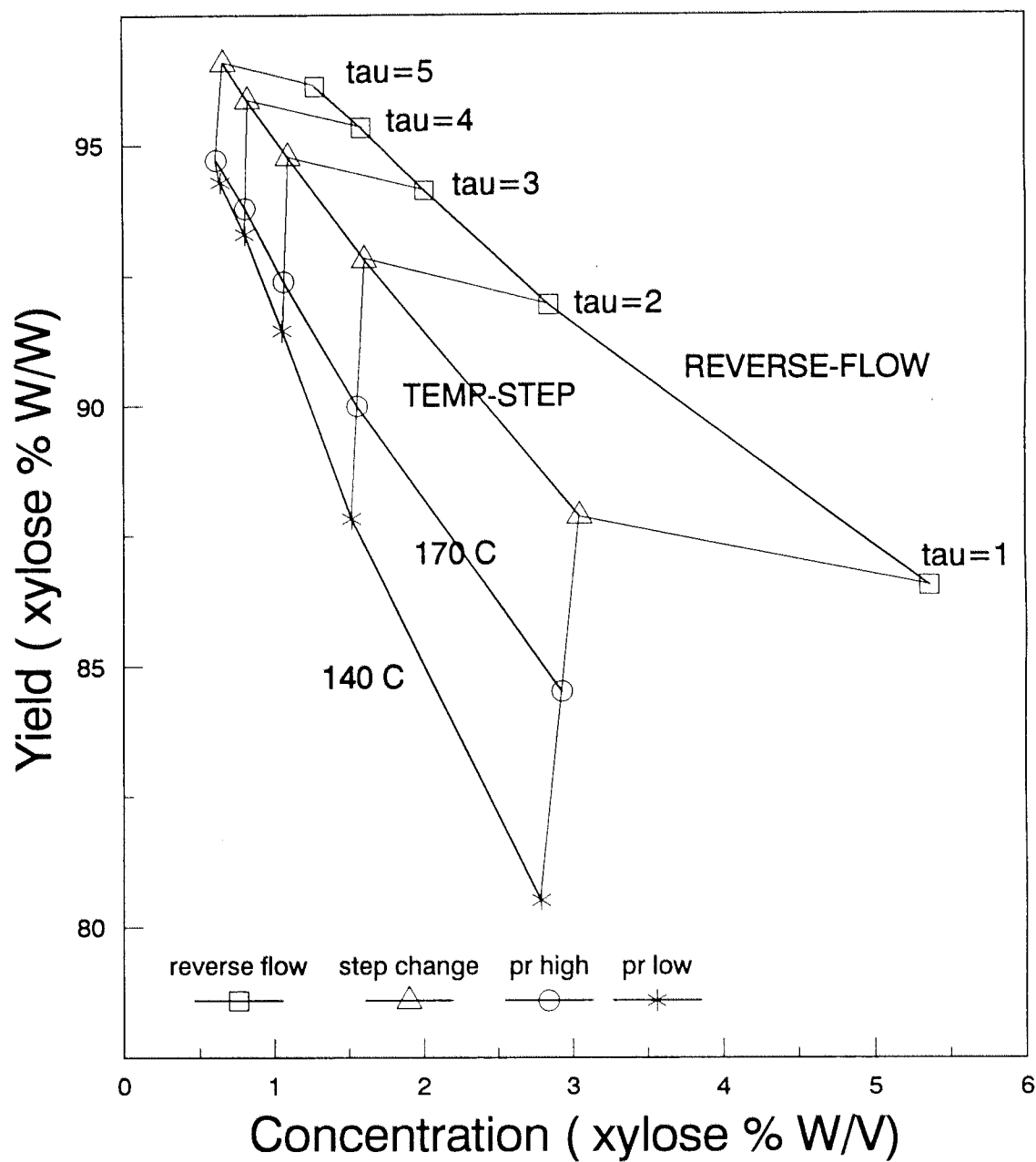
Figure 15.   Yield vs. Product Concentration under Various
              Operation Modes of Percolation (red oak)
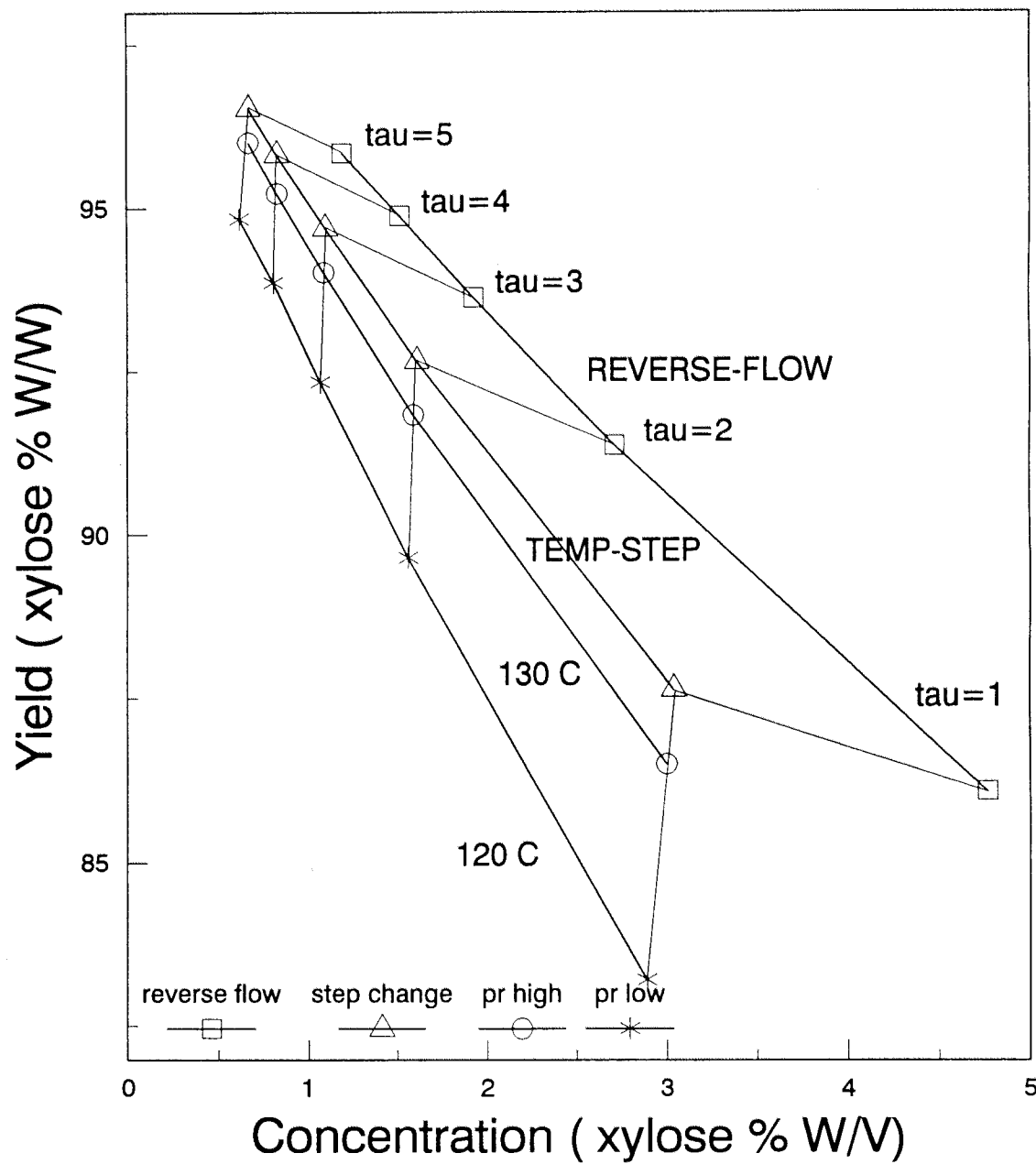
Figure 16.   Yield vs. Product Concentration under Various
Operation Modes of Percolation (aspen)
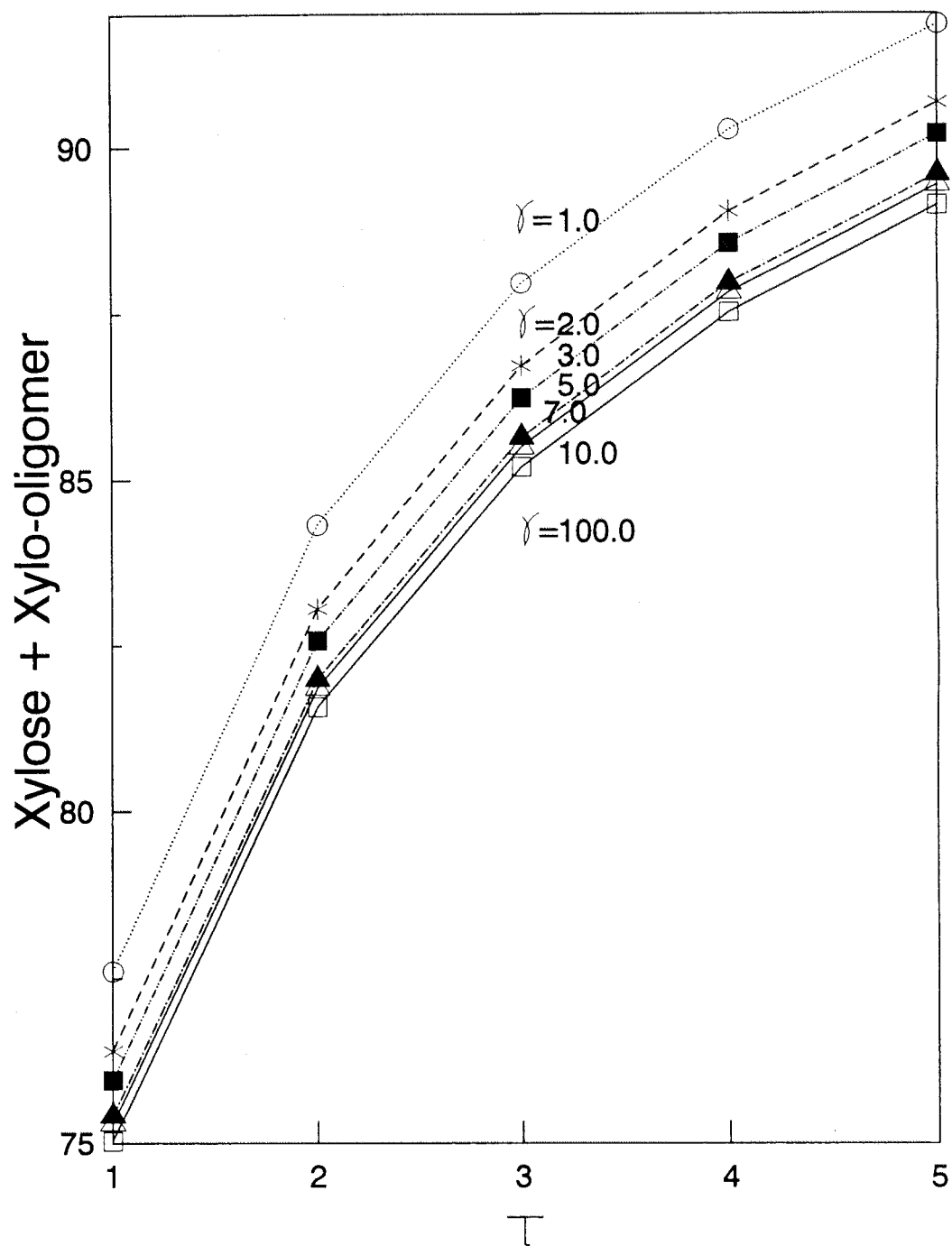
Figure 17.   Total Yield vs. τ When γ Has Different Values.
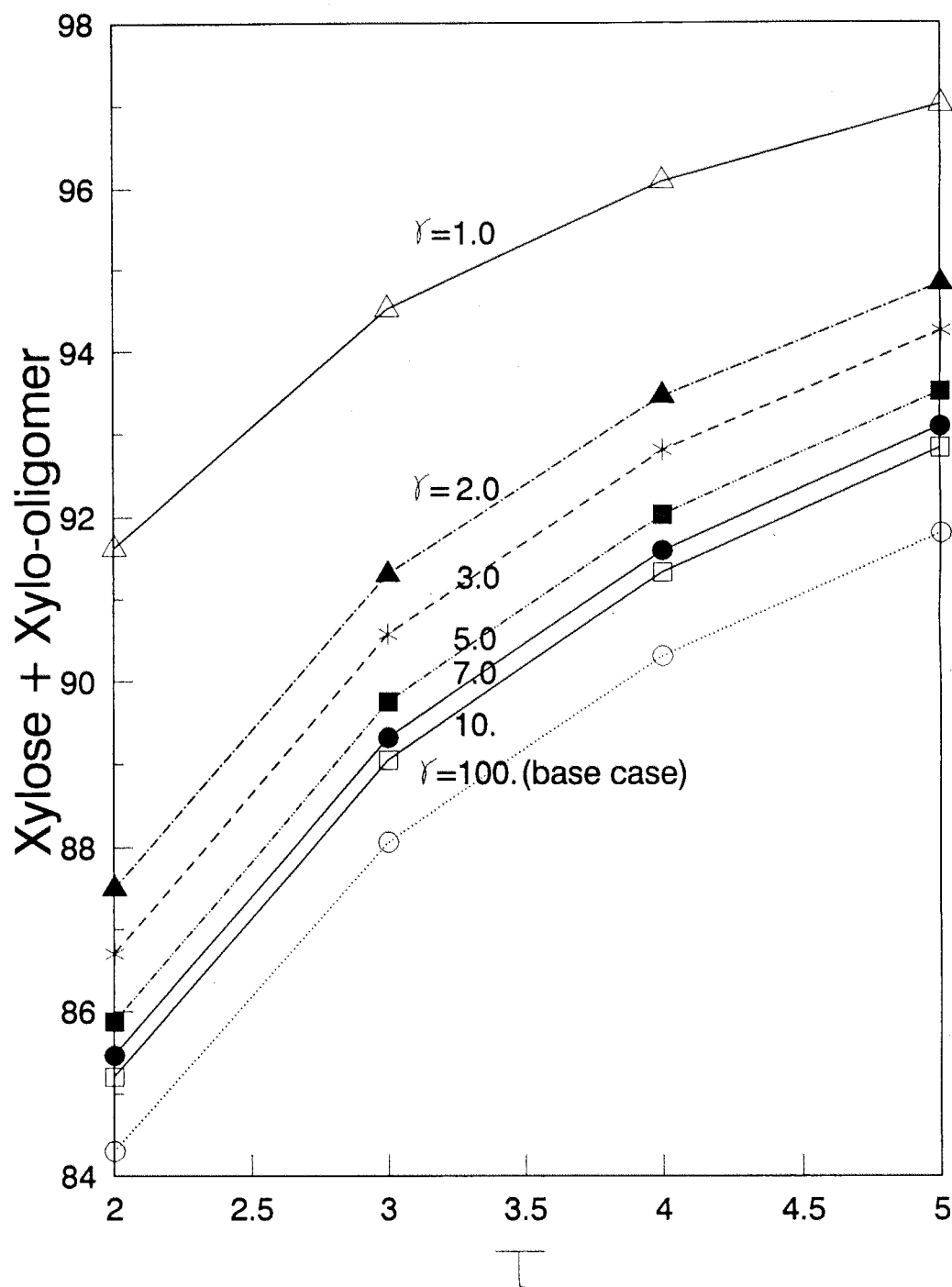
Figure 18.   Total Yield vs. τ When γ Has Different Values.

quite significant because the rate of xylo-oligomer formation has the same order of magnitude as the rate of xylo-oligomer decomposition. According to NREL's experimental data, the yield is generally 2-4% higher than that of the base case simulation results. From this, the projected γ value is speculated to be within the range of 1 and 5.

To attain a better perception of behavior of the percolation reactor, the concentrations of xylo-oligomer and xylose were calculated in relation to reactor position and reaction time. Figure 19 shows the xylo-oligomer and xylose concentration profile within a percolation reactor at $\tau = 3.0$. The upper four dotted lines indicate the xylose vs. z at $\gamma = 1,3,5$ and 100, respectively. The solid four lines indicate the xylo-oligomer vs. z curve at the same γ values. Both xylose and xylo-oligomer concentrations increase with z since both are mid-components in the sequential reaction. The xylo-oligomer curve is concave downward because the rate of xylo-oligomer formation is lower than the rate of xylo-oligomer decomposition. On the other hand, the xylose curve is concave upward because xylose formation rate is larger than the xylose decomposition rate.

Summary

The investigation to improve the reactor performance in the dilute-acid hydrolysis/pretreatment of short-rotation hard wood (hybrid poplar) is summarized as follows:

(1) The kinetics of dilute-acid hydrolysis of hybrid poplar hemicellulose were investigated by batch experimentation. The results were put into the serial/parallel reaction pattern and the kinetic parameters were statistically determined.

(2) The mathematical model for a percolation reactor was established and modifications were made to accommodate the non-ideal behavior (diffusion effect) of the reactor and variation of kinetics which includes the oligomer component.

(3) The model was put into a computer simulation program. This program capable of optimizing operation parameters for various reactor operation modes: step-change of temperature, step-change of flow rate, and two stage reverse-flow configuration.

(4) In the temperature step-change operation, three sets of temperature ranges were studied: 150 to 180 °C, 140 to 170 °C, and 165 to 185°C. In all three cases, the xylose yield with step-change in temperature was higher than that of uniform temperature at either limit. The optimum temperature difference in step-change operation was determined to be 30°C for wide range reaction temperature.

(5) The velocity ratio between the two phases of reactor operation was included as an additional adjustable parameter. Application of temperature step-change along with flow-rate step-change brought about 0.6 % improvement in product yield over the case temperature
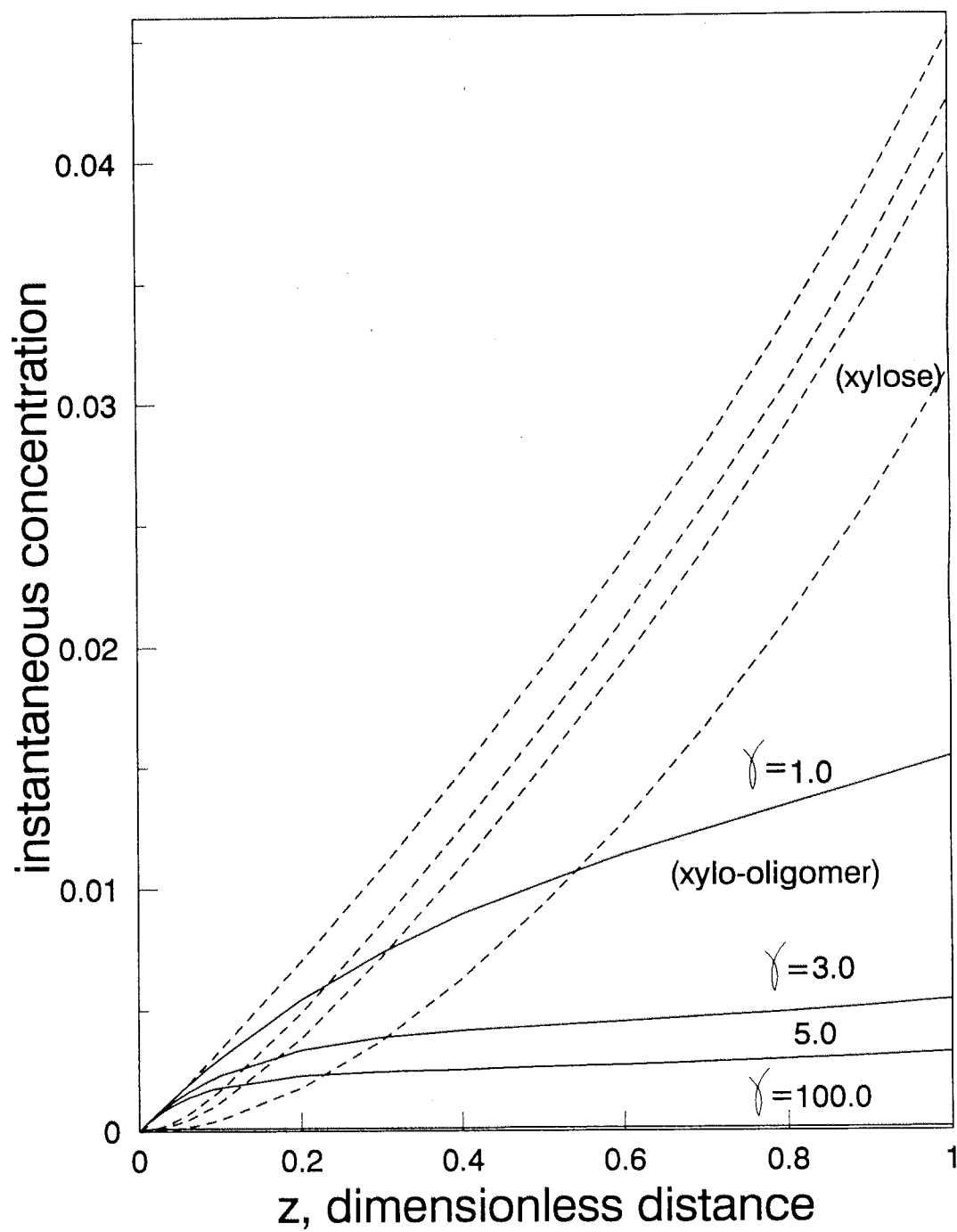
Figure 19.   Xylose and Xylo-oligomer Concentration Profile
Inside the Percolation Reactor

step-change alone.

(6) The most significant improvement was seen with the application of a two-stage reverse-flow arrangement with temperature change. Use of this application has given additional 5% improvement in product yield over that of best-case percolation reactor employing temperature step-change.

(7) The simulation results on aspen and southern red oak were quite similar to those of hybrid poplar.

(8) The effect of intra-particle diffusion on product yield was investigated. The critical wood chip sizes (above that size diffusion effect is significant) were determined to be 0.44 cm for 140-170°C step-change and 0.31 cm for 150-180°C step-change.

(9) A kinetic pattern including xylo-oligomer was incorporated into the simulation program. A sensitivity analysis was made to verify the effect of the oligomer kinetic parameter on xylose yield.

TASK II: Kinetic Study on Dilute-Acid Pretreatment of Switchgrass

The kinetic study for treatment of Switchgrass (Alamo Species) was carried out during the past year. The kinetics were modelled by a parallel hydrolysis of two fragments in hemicellulose followed by hydrolysis of oligomer, then decomposition of xylose. The kinetic parameters were determined from experimental data covering conditions of temperature(120-140°C), sulfuric acid concentration(0.46 - 2.41 wt%), and at solid:liquid ratio of (1:10.4).

EXPERIMENTAL METHODS

Sample Preparation

Switchgrass (Alamo Species) was supplied in the form of fine particles (20-60 mesh) by NREL. The xylan content measured by the NREL Standard Procedure for Carbohydrate Analysis of Biomass was 22.4 wt%(dry base). The moisture content of Switchgrass sample was determined to be 4.1 %.

The buffer capacity in Switchgrass was determined to be 3.1 mg(sulfuric acid)/g biomass(dry). The acid concentrations initially charged into the reactor were corrected accordingly, such that the four levels of acid concentrations of 0.49, 0.73, 1.22 and 2.44 wt% respectively were recalculated to 0.46, 0.70, 1.19 and 2.41 wt% respectively. The corrected values were applied in the kinetic study.

Batch Reactions

Reaction were carried out using pyrex glass tube reactors(11 mm i.d.). Glass tubes were packed with 0.5 g biomass and 5 ml acid solution, and sealed at both ends under natural gas - oxygen flame. To initial the reaction, the glass reactor ampules were placed into an oil bath (HAAKE FS2 model) for which the temperature was preadjusted to be at a temperature 50°C higher than the desired reaction temperature. After 50 seconds, the ampules were transferred into another oil bath preset at the desired reaction temperature. The temperature measured within the reactor has shown that the center section of the reactor reached a set point in 50 seconds. Temperature was measured by a thermocouple thermometer. The two oil bath procedure was done to minimize the preheating time. The time when the glass ampule was put into the second oil bath was set as the zero point of the reaction time. After being subjected to specified reaction times, the reactors were quenched in a water bath.

Sample Analysis

Analyses for sugar and oligomer were performed by HPLC(Water Associate) using RI detector and a Bio-Rad's Aminex HPX-87C column. The column temperature was set at 85°C and the mobil phase flow rate was set at 0.6 ml/min.

The kinetic data analysis was done on the basis of xylose equivalent. Where necessary the unreacted hemicellulose (xylan) was determined indirectly from material balance: unreacted xylan = initial xylan - xylose oligomer - xylose - furfural. Since the amount of furfural was much lower than other components, it was then neglected. The amount of xylose oligomer was calculated by assuming the average DP of the soluble xylose oligomer is 5.

Reaction Conditions

In order to verify the kinetics of hemicellulose hydrolysis, batch experiments were conducted according to the procedure described previously. After reviewing the results of preliminary runs, the experimental conditions were set to cover 0.46 - 2.41 wt% sulfuric acid and 120 - 140°C reaction temperature.

Kinetic Model

From our preliminary work, as shown in Fig 1, it was concluded that it would be appropriate to adopt the concept of biphasic hemicellulose such that:

H_f(xylan)   1   3   4
                    -----> O (soluble xylose oligomer)-----> X (xylose) -----> D
H_s(xylan)   2   (decomposed product)
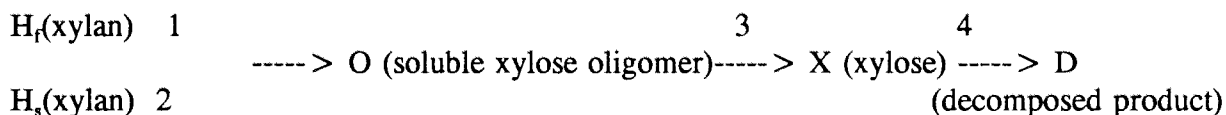
For the proposed kinetic model, the variation of individual component can be theoretically determined by the following set of differential equations:

$$\frac{dH_f}{dt} = -k_1 A^{n1} H_f \qquad\qquad (1)$$

$$\frac{dH_s}{dt} = -k_2 A^{n2} H_s \qquad \textbf{(2)}$$

$$\frac{dO}{dt} = k_1 A^{n1} H_f + k_2 A^{n2} H_s - k_3 A^{n3} O \qquad \textbf{(3)}$$

$$\frac{dX}{dt} = k_3 A^{n_3} O - k_4 A X \qquad \textbf{(4)}$$

with initial conditions:

> at $t = 0$, $H_f = F_f H_0$
> at $t = 0$, $H_s = (1 - F_f) H_0$
> at $t = 0$, $O = 0$
> at $t = 0$, $X = 0$

where:

> F_f = fast hydrolyzable fraction,
> H_0 = initial xylan content.

The analytical solutions for equations (3) and (4) were obtained as follows:

$$O = a_{11} \left(e^{-c_2 t} - e^{-c_5 t} \right) + a_{12} \left(e^{-c_4 t} - e^{-c_5 t} \right) \qquad \textbf{(5)}$$

$$X = a_{21} \left(e^{-c_2 t} - e^{-c_6 t} \right) + a_{22} \left(e^{-c_4 t} - e^{-c_6 t} \right) + a_{23} \left(e^{-c_5 t} - e^{-c_6 t} \right) \qquad \textbf{(6)}$$

where:

$$c_1 = k_1 A^{n1} F_f H_o$$

$$c_2 = k_1 A^{n1}$$

$$C_3 = k_2 A^{n2} (1 - F_f) H_o$$

$$C_4 = k_2 A^{n2}$$

$$C_5 = k_3 A^{n3}$$

$$C_6 = k_4 A$$

$$a_{11} = \frac{C_1}{C_5 - C_2}$$

$$a_{12} = \frac{C_3}{C_5 - C_4}$$

$$a_{21} = \frac{C_1 C_5}{(C_5 - C_2)(C_6 - C_2)}$$

$$a_{22} = \frac{C_3 C_5}{(C_5 - C_4)(C_6 - C_4)}$$

$$a_{23} = - \frac{C_5}{C_6 - C_5} \left(\frac{C_1}{C_5 - C_2} + \frac{C_3}{C_5 - C_4} \right)$$

To determine the kinetic parameters in above two equations simultaneously, the SAS

NLIN Program was used to regress the following objective function:

$$Y = O^2 + X^2 \qquad\qquad\qquad (8)$$

RESULTS

The experimental data at 120, 130, 135 and 140°C were used to fit equation (8). During the regression,   The best fitting F_f value was found to be 0.65. Similarly, the best fitting values for n_1, n_2 and n_3 were found to be 1.2, 1.2 and 1.6 respectively.

The k_4 data were taken from the work of Kim et al (12). Having the xylose decomposition data $k_4 A$ value for various reaction conditions from S. B. Kim, the remaining 12 parameters (four each for k_1, k_2 and k_3 at four different temperature level) were determined employing data from 20 experimental runs. The parameter estimation was performed by nonlinear regression analysis. The resulting kinetic parameters are shown in Table 1. The statistical analysis has shown the upper limit of the standard deviations of all the kinetic parameters was less than 14% (see Appendix 1 "Modelling result of Switchgrass Hydrolysis").

By applying Arrhenius equation for k_1, k_2 and k_3, it is shown in Figure 2 that the resulting kinetic parameters were in good agreement with Arrhenius equation. Table 2 is the activation energy for reaction 1, 2 and 3. Of particular significance in this result is that the oligomer reaction is more sensitive to temperature and concentration than the hydrolysis reactions. Thus, the higher the temperature and acid concentration, the higher yield of xylose is expected. The comparison between the predicted reaction progress calculated from the model and associated parameters, and the actual experimental data are shown in Appendix 2. The model prediction was generally in good agreement with experimental data, thus confirming that the proposed model is valid for hydrolysis of Switchgrass hemicellulose.

SUMMARY

The significant findings in the kinetic study on dilute-acid pretreatment of Switchgrass as follows:

1. The hemicellulose in Switchgrass is of biphasic.

2. Activation energy for hydrolysis is about the same as that of xylose decomposition.

3. Oligomer hydrolysis reaction is more sensitive to temperature and acid concentration than hydrolysis of hemicellulose to oligomer..

4. The higher the temperature and acid concentration, the less amount of oligomer is expected.

TASK III: Determination of Thermal Diffusivity for Hybrid Poplar

The experimental work concerning the thermal diffusivity determination for hybrid poplar was carried out. The thermal diffusivities of hybrid poplar were experimentally determined in the longitudinal and radial directions.

HEAT TRANSFER THEORY

A heat balance within a differential segment of the wood chip results in an unsteady state conduction equation,

$$\frac{\delta T}{\delta t} = \alpha \frac{\delta T^2}{\delta x^2} \tag{1}$$

with the boundary conditions of

$$x = 0, \quad \delta T/\delta t = 0 \tag{2}$$
$$x = L, \quad \delta T/\delta t = -h(T-Ts)/k \tag{3}$$

and the initial condition

$$t = 0, \quad T = To \tag{4}$$

where

T = Temperature
t = Time
x = Thickness measured from the center
α = Thermal diffusivity
Ts = Surrounding water temperature
To = Initial temperature
k = Thermal conductivity
h = Heat transfer coefficient
L = Half the thickness of the slab

Using the following transformation, equations (1) through (4) become dimensionless

$$z = x/L$$
$$\tau = t/L^2$$
$$\theta = (T - Ts)/(To - Ts)$$

and equation (1) through (4) become

$$\frac{\delta \theta}{\delta \tau} = \frac{\delta \theta^2}{\delta z^2} \tag{5}$$

$$z = 0, \quad \delta\theta/\delta z = 0 \qquad\qquad\qquad (6)$$
$$z = 1, \quad \delta\theta/\delta z + Nu.\theta = 0 \qquad\qquad (7)$$
$$\tau = 0, \quad \theta = 1 \qquad\qquad\qquad\qquad (8)$$

where

$$Nu = hL/k$$

The Nu values were large enough to assume the boundary condition of T = Ts at x = L. The general analytical solution to equation (5), after application of corresponding boundary conditions and initial condition, becomes

$$\theta - 2 \sum_{n-0}^{\infty} \frac{(-1)^n}{\lambda_n} \exp(-\lambda_n^2 \tau) \cos(\lambda_n z) \qquad (9)$$

where
$$\lambda_n = (2n+1)\pi/2$$

This solution is graphically presented in figure 1 showing the variation of θ as a function of dimensionless distance (z) and time (τ).

DETERMINATION OF THERMAL DIFFUSIVITIES

Experiments were designed to measure the change of temperature inside the wood samples. This temperature profile was later used in a nonlinear regression to determine the thermal diffusivities. In these experiments, wood was cut into rectangular pieces of various sizes. The ratio of the size of the wood in the direction in which thermal diffusivity was determined to the size in the other directions was 1 to 4, and the non-heat-transfer surfaces were covered by silicone sealant. This was done to minimize heat conduction through non-heat-transfer sides, thus forcing a unidirectional flow of heat. Wood was impregnated in water for 24 hours before being used in experiments. Moisture content of wood was found to be 60.8%. The thermal diffusivity was determined in longitudinal (parallel to grain) and radial (across grain) directions.

The thermal diffusivities were determined over the temperature range from 31-96 °C. The wood sample was subjected to a step-change of temperature by inserting it into a waterbath. A thermocouple was inserted into the wood chip. The temperature was measured at the center point of the chip. Figure 2 illustrates the experimental setup. Equation (9) was used as a model in a SAS nonlinear regression program to determine the thermal diffusivities. The first eight terms of the infinite series were used in the calculations.

The output from SAS for Hybrid Polar is presented in Table 1 and 2. The thermal diffusivities in the longitudinal and radial directions were found to be $3.1 \times 10^{-7} \pm 0.016 \times 10^{-7}$ m^2/s and $1.9 \times 10^{-7} \pm 0.011 \times 10^{-7}$ m^2/s respectively in the temperature range from 31 - 96 °C. The comparisons between the predicted temperature profile calculated from equation (9) with associated thermal diffusivities and the actual experimental data are shown in Figure 3. The prediction is in good agreement with the experimental data.

Equation (9) was used to determine the thermal diffusivities at a given temperature. Figure 4 shows that the thermal diffusivities of wood in radial direction are quite close to those of water, and those of wood in longitudinal direction are higher. The thermal diffusivities of wood in both directions increase slightly as the surrounding water temperature increases.

In actual acid hydrolysis reactions, wood chips are usually cut into small pieces of random sizes. The direction with respect to the grain is also random. Therefore the values of the thermal diffusivities obtained for the two different directions were averaged into 2.5×10^{-7} m^2/s in the temperature range from 31 to 96 °C.

SUMMARY

1. The thermal diffusivities of Hybrid Polar wood in longitudinal and radial directions were determined to be $3.1 \times 10^{-7} \pm 0.016 \times 10^{-7}$ m^2/s and $1.9 \times 10^{-7} \pm 0.011 \times 10^{-7}$ m^2/s respectively within the temperature range of 31 - 96 °C.

2. The predicted temperature profiles calculated from equation (9) with associated thermal diffusivities are in good agreement with the experimental data.

3. The thermal diffusivities of Hybrid Polar in both directions increase slightly as a function of temperature.

Nomenclatures

A	hemicellulose
A_i	frequency factor for rate constant k_i, minutes^{-1}
B	xylose and soluble xylose oligomer
C	decomposed product
C_A, C_{AF}, C_{AS}	concentration of xylan as a xylose
C_B, C_{BF}, C_{BS}	concentration of xylose
C_{Ho}	(total xylan as a xylose)/(total liquid volume)
C_P	average product concentration, w/v %
D_e	effective diffusivity, cm^2/sec
d_{cw}	the density of crystalline wood, 1.54 g/ml
E_i	activation energy for rate constant k_i
H_F,H_S	the fraction of fast and slow hemicellulose
k_i	reaction rate constant, minutes^{-1}
k	reaction rate constant
k_o	frequency factor
L	reactor length, cm
N_i	acid concentration exponent
P	packing factor
R	universal gas constant
S_B, S_{BF}, S_{BS}	C_B / C_{Ao}, C_{BF} / C_{AFo}, C_{BS} / C_{ASo}
t	time, minutes
T	absolute temperature,$^{\circ}$K
u	velocity inside reactor, cm / min
x	distance coordinate along reactor length, cm
Y_B, Y_{BF}, Y_{BS}	yields of B for uniform temperature operation: overall; fast fraction; slow fraction
Y_{BSTEP}	yields of B for step change operation
z	x / L

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Greek

α_i	k_3/k_i, $i = 1,2$
α'	$\alpha(1 + \eta P\theta)$
β_{opt}	optimum β (corresponding to maximum yield)
β_F	$k_1 L/u$
β_S	$k_2 L/u$
γ	k_4/k_i, $i = 1,2$
ϵ	void fraction in reactor
η	overall effectiveness factor
Θ	porosity within solid
ρ	τ_1/τ
τ	tu/L

Subscripts

A	denotes component A
B	component B
F	fast xylan
i	reaction no.
oli	xylo-oligomer
opt	optimum
S	slow xylan
o	value at $t = 0$
1	indicates early phase in step change process
2	latter phase in step change process

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APPENDICES

APPENDIX A

The Algorithm for Kinetic Parameter Determination

The Algorithm for Kinetic Parameter Determination

i) Assume the best fit model like the below equation

$H0 = 21$

$K3 = 1.01*10^{11}*A^{0.48}*exp(-25330/R/T)$

$TERM1 = (1-FD)*H0*K1/(K3-K1)*[EXP(-K1*T)-EXP(-K3*T)]$

$TERM2 = FD*H0*K2/(K3-K2)*[EXP(-K2*T)-EXP(-K3*T)]$

$model = term1 + term2$

ii) By use of the SAS non-linear data regression procedure,
determine the parameters, FD, K1, and K2.

iii) Do the procedure (i) for eleven sets of Y vs. time to get
each corresponding parameter.

iv) Take the average of FD values.
Let AFD = the average FD values.

v) By use of the SAS non-linear data regression procedure,
determine K1, K2 again. (FD = AFD)

vi) Determine the temperature dependent term and the acid concentration
dependent term by using the results of procedure(v).

APPENDIX B

The Sample SAS Output Data

```
+OUTPUT-----------------------------------------------------------------------
+|Command ===>
  ||
  ||                        hemicellulose kinetics
  ||                                            09:47 Friday, February 19, 1993
  ||
  |Non-Linear Least Squares Iterative Phase   Dependent Variable Y   Method: DUD
  ||     Iter              K1              K2              D Sum of Squares
  ||       8         0.165801        0.018100      6.088290        0.149877
  ||       9         0.165801        0.018100      6.088290        0.149877
  ||NOTE: Convergence criterion met.
  ||
  ||
  ||
  ||     Non-Linear Least Squares Summary Statistics     Dependent Variable Y
  ||
  ||       Source                  DF Sum of Squares      Mean Square
  ||
  ||       Regression               3   1359.1265510     453.0421837
  ||       Residual                 8      0.1498770       0.0187346
  ||       Uncorrected Total       11   1359.2764281
  ||
  ||       (Corrected Total)       10     75.8886445
  ||
  ||
  ||       Parameter     Estimate    Asymptotic           Asymptotic 95 %
  ||                                 Std. Error         Confidence Interval
  ||                                                   Lower          Upper
  ||         K1    0.165800804 0.00579684188  0.1524331340  0.1791684746
  ||         K2    0.018099564 0.00136488004  0.0149521146  0.0212470134
  ||         FD    6.088289899 0.33450108426  5.3169215732  6.8596582238
```

APPENDIX C

Sample Output of Percolation Simulator

-----GIVEN DATA-----

LOW T(C)	HIGH T(C)	ACID CONC.(%W/V)	REACTOR LENGTH(CM)	W=
140.0	170.0	0.83370	5.0800	1.0

-----RESULTS-----

#1 XYLOSE YIELD(%), DECOMPOSED(%)& HEMICELLULOSE UNREACTED(%)

	UNI LOW			UNI HIGH			STEP CHANGE		
TAU	YIELD	DECOMP	HC	YIELD	DECOMP	HC	YIELD	CONC.	DECOMP	HC
1	69.38	10.76	19.86	73.61	11.41	14.97	72.81	2.53	15.35	11.85
2	75.37	10.27	14.36	79.94	10.94	9.12	82.14	1.43	16.27	1.58
3	79.05	10.78	10.16	83.52	10.25	6.23	86.09	1.00	12.83	1.08
4	81.69	10.37	7.95	85.87	9.29	4.84	88.52	0.77	10.75	0.73
5	83.65	9.82	6.53	87.56	8.18	4.26	90.17	0.63	9.23	0.59

#2 CELLULOSE HYDROLYZED(%) & GLUCOSE DECOMPOSED(%)

	UNI LOW		UNI HIGH		STEP CHANGE	
TAU	C.H.	G.D.	C.H.	G.D.	C.H.	G.D.
1	0.483	0.041	2.127	0.269	2.425	0.425
2	0.844	0.063	3.676	0.409	5.836	1.831
3	1.263	0.095	4.871	0.486	6.958	1.726
4	1.561	0.109	5.660	0.498	7.911	1.728
5	1.799	0.116	6.051	0.460	8.535	1.600

#3 OPTIMAL RXN TIME(MINS)& VOLUMETRIC FLOW RATE(CC/MINS)

	UNI LOW		UNI HIGH		STEP CHANGE			
TAU	R.T.	VFR	R.T.	VFR	RT1.	RT2.	VFR1	VFR2
1	65.424	0.327	8.451	2.531	2.699	9.568	1.743	1.743
2	114.492	0.374	14.720	2.906	29.005	22.789	0.826	0.826
3	171.738	0.374	19.627	3.269	29.768	27.478	1.121	1.121
4	212.628	0.402	22.898	3.736	34.021	31.404	1.308	1.308
5	245.340	0.436	24.534	4.359	34.075	34.075	1.569	1.569

#4 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM

TAU	PRODUCT CONC.	PRODUCT YIELD	RHO	OPTIMAL BETA
1	3.492	71.871	0.220	0.900
2	2.480	80.032	0.560	1.900
3	1.876	84.309	0.520	1.400
4	1.452	87.028	0.520	1.200
5	1.234	88.852	0.500	1.000

```
        -----GIVEN DATA-----
-------------------------------------------------------------------
LOW T(C)    HIGH T(C)    ACID CONC.(%W/V)    REACTOR LENGTH(CM)  W=
-------------------------------------------------------------------
     150.0      180.0          0.83370             5.0800          2.5
-------------------------------------------------------------------

        -----RESULTS-----
#1 XYLOSE YIELD(%), DECOMPOSED(%)& HEMICELLULOSE UNREACTED(%)
-------------------------------------------------------------------
          UNI LOW           UNI HIGH            STEP CHANGE
TAU  YIELD DECOMP HC    YIELD DECOMP HC    YIELD  CONC. DECOMP HC
-------------------------------------------------------------------
  1  70.78  10.88 18.34 75.04 11.80 13.16 76.28  2.65  19.14  4.58
  2  76.92  10.75 12.33 81.35 10.98  7.67 83.69  1.45  14.29  2.02
  3  80.64  10.59  8.77 84.80  9.79  5.41 87.26  1.01  11.53  1.21
  4  83.20   9.97  6.83 87.03  8.65  4.32 89.46  0.78   9.66  0.89
  5  85.09   9.45  5.46 88.62  7.72  3.66 90.96  0.63   8.34  0.70
-------------------------------------------------------------------

#2 CELLULOSE HYDROLYZED(%) & GLUCOSE DECOMPOSED(%)
-------------------------------------------------------------------
          UNI LOW           UNI HIGH           STEP CHANGE
TAU   C.H.      G.D.     C.H.      G.D.     C.H.      G.D.
-------------------------------------------------------------------
  1   0.802    0.078    3.391    0.491    4.522     1.144
  2   1.445    0.127    5.644    0.698    6.819     1.376
  3   2.023    0.167    7.089    0.749    8.394     1.438
  4   2.447    0.185    8.012    0.729    9.523     1.392
  5   2.824    0.198    8.678    0.692   10.593     1.344
-------------------------------------------------------------------

#3 OPTIMAL RXN TIME(MINS)& VOLUMETRIC FLOW RATE(CC/MINS)
-------------------------------------------------------------------
     UNI LOW       UNI HIGH          STEP CHANGE
TAU  R.T.    VFR    R.T.    VFR    RT1.    RT2.    VFR1    VFR2
-------------------------------------------------------------------
  1   31.655  0.676   4.626  4.623   8.328   5.922   0.925   2.311
  2   57.222  0.748   7.792  5.489  12.711   9.039   1.211   3.029
  3   80.354  0.798   9.862  6.506  15.779  11.220   1.464   3.660
  4   97.399  0.878  11.201  7.638  16.558  12.857   1.757   4.392
  5  112.618  0.950  12.175  8.783  15.523  14.488   2.067   5.167
-------------------------------------------------------------------

#4 FINAL PRODUCT CONC.(%) & PRODUCT YIELD(%) WITH REVERSE STREAM
-------------------------------------------------------------------
TAU    PRODUCT CONC.   PRODUCT YIELD   OPTIMAL RHO    OPTIMAL BETA
-------------------------------------------------------------------
  1       4.701           73.380          0.360          3.800
  2       2.673           81.775          0.360          2.900
  3       1.883           85.776          0.360          2.400
  4       1.445           88.278          0.340          2.000
  5       1.159           90.033          0.300          1.700
-------------------------------------------------------------------
```

APPENDIX D

FORTRAN SOURCE CODE FOR

TWO-STAGE PERCOLATION TYPE

PRETREATMENT REACTOR

PROGRAM TSPPR

```
C  TSPPR (Two Stage Percolation type Pretreatment Reactor)
C------------------------------------------------------------
C
C
C                       ARRAYS
C
C------------------------------------------------------------
blh (60):               beta value of step change
cy (10):                maximum concentration
dbeta (10):             beta value at maximum yield
dbth (10):              uniform high beta optimum
dbtl (10):              uniform low beta optimum
dcl (10):               celluluse loss of step change
dclLo (10):             cellulose hydrlyzed of low temp eactor
ddHi (10):              cellulose hydrlyzed of high temp reactor
dgh (10):               uniform high glucose decomposed
dgl (10):               uniform low glucose decomposed
dglh (10):              step change glucose decomposed
                        in high temperature reactor
dhhi (10):              hemicellulose hydrolyzed in high  reactor
dhlh (10):              hemicellulose hydrolyzed in step change
dhlo (10):              hemicellulose hydrolyzed in low temperature
                        reactor
dtmhi (10):             actual time of uniform high
dtmlo (10):             actual time of uniform low
dtm1 (10):              actual time of low Temperature reaction
dtm2 (10):              actual time of high reaction
dvel (10):              linear velocity of high Temperature
                        reaction
dvelhi (10):            linear velocity of high temperature reactor
dvello (10):            linear velocity of low temperature reactor
dvell (10):             linear velocity of low Temperature reaction
dxh (10):               uniform high xylose decomposed
dxl (10):               uniform low xylose decomposed
dxlh (10):              step change xylose decomposed
gyh (10):               uniform high glucose yield
gyl (10):               uniform low glucose yield
gylh (10):              step change glucose
rho (10):               rho value at maximum yield
xhy (10):               maximum yield of uniform high
xly (10):               maximum yield of uniform low
xy (10):                overall maximum of step change
yh (500):               uniform high yield 0.2 < beta < 5.0
yl (500):               uniform low yield 0.2 < beta < 5.0
ylh (500):              step change yield 0.9 < beta < 3.0
y2t (60):               local maximum of step change
```

```
C------------------------------------------------------------
C
C                        Constants
C
C------------------------------------------------------------
-       a       a cross sectional area of a percolator
        c       sulfuric acid concentration
        ch0     (total xylan as a xylose)/(total liquid volume)
        tl      temperature low limit
        th      temperature high limit
        w       the ratio of v1 to v2
        tau     dimensionless time
        be      beta value
```

```
C----------------------------------------------------------
C
C       MAIN PROGRAM OPTIMA FOR DATA INPUT,
C       SUB-PROGRAMS CALL, AND RESULTS OUTPUT.
C----------------------------------------------------------
        intrinsic exp
        dimension ylh(500),y2t(60), blh(60), xy(10), rho(10),obeta(60)
        dimension cy(10), yl(500),yh(500),xly(10),dvel2(10)
        dimension xhy(10),dtm1(10),dtm2(10),dvel1(10),dcl(10)
        dimension dtmlo(10),dtmhi(10),dvello(10),dvelhi(10)
        dimension gyl(10),gyh(10),dcllo(10),dclhi(10),gylh(10)
        dimensiondgl(10),dgh(10),dglh(10),dxl(10),dxh(10)
        dimension dbtl(10),dbth(10),dhlo(10),dhhi(10),dhlh(10)
        dimension dqvlo(10),dqvhi(10),dq1(10),dq2(10)
        dimension dfy(10),dfc(10), dxlh(10)
        open(unit=7,file='input.dat ',status='unknown')
        open(unit=8,file='output.dat',status='unknown')
C       .....ASSIGN INPUT DATA TL, TH, C, RlEN, CH0, W, & A....
        data tl, th, c ,rlen/140., 170., 0.8337,5.08/
        data ch0,w,a/3.471,0.5,4.21/
        print * , tl,th,c,ch0,w
        write(8,5)
        write(8,10)
        write(8,20)
        write(8,30) tl,th,c,rlen,w
    5 format(1x,t5,"output.dat",/)
   10 format(/,1x,t10,"--GIVEN DATA-----",/,t1,79(1h-))
   20 format(t2,"LOW T(C)",t15,"HIGH T(C)",t30,' ACID CONC.
       +(%W/V)',t50,'REACTORLENGTH(CM)',t70,'w=',/,t1,79(1h-))
   30 format(t2,f10.1,t13,f10.1,t30,f10.5,t50,f10.4,t70,
       +f3.1,/,1x,79(1h-),/)
C       .....DO LOOP WITH TAU FROM 1.0 TO 5.0.....
        do 100 k=1,5
        tau=float(k)
C       .....Calculate Uniform High and Uniform Low Yield.....
C       .....DO LOOP WITH BETA1 FROM 0.2 TO 5.0.....
        do 310 i=1,59
        ip1=i+1
        be=float(ip1)/10.
C       .....CALL SUBFUNCTION  YLDF TO CALCULAT4E YIELD.....
        yl(i)=yldf(tau,1.0,be,tl,th,c,1.)*100.
        beo5=be/5.0
        yh(i)=yldf(tau,0.0,beo5,tl,th,c,1.)*100.
        print *, yl(i),yh(i)
  310   continue
C       .....CALL SUBROUTINE SEEK1 TO SEEK MAXIMUM YIELD WHEN
C       RHO IS GIVEN.....
        call seek1(yl,btl,amaxl,59)
        print *,amaxl
        dbtl(k)=btl
```

```
      print*, "btl",btl
      xly(k)=amaxl
      gyl(k)=gyldf(tau,1.0,btl,tl,th,c,1.0)*100.
      print*,"gyl(k)=", gyl(k)
      call rxncon1(rlen,tau,btl,tl,c,tmlo,vello,qvlo,a)
      print *,"tmlo=", tmlo
      dtmlo(k)=tmlo
      dvello(k)=vello
      dqvlo(k)=qvlo
      call cellr1(tl,c,tmlo,cllo)
      dcllo(k)=cllo
      dgl(k)=dcllo(k)-gyl(k)
      call hemic1(tl,c,tmlo,hlo)
      dhlo(k)=hlo
      dxl(k)=dhlo(k)-xly(k)
      call seek1(yh,bth,amaxh,59)
      rbth=bth*ak1(th,c)/ak1(tl,c)/5.0
      dbth(k)=rbth
      xhy(k)=amaxh
      btho5=bth/5.0
      print*, "bth= ", bth
      gyh(k)=gyldf(tau,0.0,btho5,tl,th,c,1.0)*100.
      print*, "gyh(k)=", gyh(k)
      call rxncon1(rlen,tau,rbth,th,c,tmhi,velhi,qvhi,a)
      print*,"tmhi=  " , tmhi
      dtmhi(k)=tmhi
      dvelhi(k)=velhi
      dqvhi(k)=qvhi
      call cellr1(th,c,tmhi,clhi)
      dclhi(k)=clhi
      dgh(k)=dclhi(k)-gyh(k)
      call hemic1(th,c,tmhi,hhi)
      dhhi(k)=hhi
      dxh(k)=dhhi(k)-xhy(k)
C
C     .....Calculate Step Change yield.....
C     .....DO LOOP WITH RHO FROM 0.20, TO 0.80.....
      do 200 m=1,30
      mp20=m*2 + 20
      frho=float(mp20)/100.
C
C     .....DO LOOP WITH BETA1 FROM .2 TO 4.3.....
      do 300 i=1,42
      ip1=i+1
      be=float(ip1)/10.
C     .....CALL SUBFUNCTION  YLDF TO CALCULAT4E YIELD.....
      ylh(i)=yldf(tau,frho,be,tl,th,c,w)*100.
 300  continue
C     .....CALL SUBROUTINE SEEK1 TO SEEK MAXIMUM YIELD WHEN
C     RHO IS GIVEN.....
```

```
          call seek1(ylh,btlh,amax,42)
          y2t(m)=amax
          blh(m)=btlh
          print *, "amax", amax, "btlh= ",btlh
c         if(m.eq.1)then
c         goto 200
c         elseif(y2t(m-1).ge.y2t(m))then
c         xy(k)=y2t(m-1)
c         cy(k)=ch0*xy(k)/tau/100.
c         rho(k)=float(2*m+18)/100.
c         obeta(k)=blh(m-1)
c         goto 99
c         endif
  200     continue
C       .....CALL SUBROUTINE SEEK2 TO SEEK MAXIMUM YIELD IN
TERMS OF RHO &
C       BETA.....
          call seek2(y2t,mth,amax,30)
          xy(k) = amax
          cy(k)=ch0*amax/tau/100.
          rho(k) = float(mth*2+20)/100.
          obeta(k)=blh(mth)
C         write(8,*) tau, xy(k),rho(k),obeta(k)
          rrho=rho(k)
          be1=obeta(k)
          print*,"tau=",tau,"yield=",xy(k),"rho=",rho(k),"beta=",obeta(k)
          call rxncon(rlen,tau,be1,rrho,tl,c,w,tm1,tm2,vel1, vel2, q1,q2,a)
          time1=tm1
          time2=tm2
          call cellr(tl,th,c,time1,time2,cl)
          dtm1(k)=tm1
          dtm2(k)=tm2
          dvel1(k)=vel1
          dvel2(k)=vel2
          dq1(k)=q1
          dq2(k)=q2
          dcl(k)=cl
          gylh(k)=gyldf(tau,rrho,be1,tl,th,c,w)*100.
          dglh(k)=dcl(k)-gylh(k)
          call hemic2(tl,th,c,time1,time2,hlh)
          dhlh(k)=hlh
          dxlh(k)=dhlh(k)-xy(k)
          print*, rrho,be1,tl,th,c,"w=",w
          yr1=fyr1(tau,rrho,be1,tl,th,c,w)*100.
          tau1=tau*rrho
          cr1=ch0*yr1/tau1/100.
C
          yr2=fyr2(tau,rrho,be1,tl,th,c,w)*100.
          tau2=tau*(1.-rrho)
          cr2=ch0*yr2/tau2/100.
```

```fortran
      call  recycle(tl,c,vel1,rrho,rlen,yr2,yr1, cr2, cr1, fy, fc)
      dfy(k)=fy
      dfc(k)=fc
100   continue
C     .....PRINT OUT THE CALCULATION RESULTS.....
      call output1(xly,dxl,xhy,dxh,xy,cy,dxlh)
      call output2(dcllo,dgl,dclhi,dgh,dcl,dglh)
C     call    output3(dtmlo,dvello,dtmhi,dvelhi,dtm1,dtm2,dvel1, dvel2)
      call output4(dtmlo,dqvlo,dtmhi,dqvhi,dtm1,dtm2,dq1,dq2)
      call output5(dfy,dfc,rho,obeta)
      stop
      end
C------------------------------------------------------------
C              .....THE END OF MAIN PROGRAM.....
C------------------------------------------------------------
```

```
C-----------------------------------------------------------
C
C        Subroutine to Calculate Yield
C
C-----------------------------------------------------------
        function  gyldf(tau,rho,be,temp1,temp2,conc,w)
        t1=temp1
        t2=temp2
        c=conc
        a1=ak5(t1,c)/ak4(t1,c)
        a2=ak5(t2,c)/ak4(t2,c)
        b1=be*ak4(t1,c)/ak1(t1,c)
        b2=be*ak4(t2,c)/ak1(t1,c)/w
        tau1=tau*rho
        tau2=tau*(1.0-rho)
        c1=b1*tau1
        print*,"a1=",a1,"b2=",b2
        if(c1.gt.50.)then
        ec1=0.0
        elseif(tau1.eq.0.)then
        ec1=1.0
        else
        ec1=exp(-c1)
        endif
        call dfeq(tau1,a1,b1,yield,9001)
        y1=yield
        call dfeq(tau2,a2,b2,yield,9001)
        y2=ec1*yield
        gyldf=y1+y2
        return
        end
```

```
C---------------------------------------------------------
C       Subprogram to Calculate Yield
C       When Rho and Beta are Given
C---------------------------------------------------------
        function yldf(tau,rho,be,temp1,temp2,conc,w)
        t1=temp1
        t2=temp2
        c=conc
C       .....CALCULATE THE COEFFICENTS.....
        ae1=ak3(t1,c)/ak1(t1,c)
        ad1=ak3(t1,c)/ak2(t1,c)
        ae2=ak3(t2,c)/ak1(t2,c)
        ad2=ak3(t2,c)/ak2(t2,c)
        be1=be
        bd1=be1*ak2(t1,c)/ak1(t1,c)
        be2=be1*ak1(t2,c)/ak1(t1,c)/w
        bd2=be1*ak2(t2,c)/ak1(t1,c)/w
        ue1=ae1*be1
        ud1=ad1*bd1
        tau1=tau*rho
        tau2=tau*(1.-rho)
        ce1=be1*tau1
        cd1=bd1*tau1
        if(ce1.gt.50.) then
        ece1=0.0
        elseif(tau1.eq.0.0) then
        ece1=1.0
        else
        ece1=exp(-ce1)
        endif
        if(cd1.gt.50.) then
        ecd1=0.0
        elseif(tau1.eq.0.0) then
        ecd1=1.0
        else
        ecd1=exp(-cd1)
        endif
C       .....CALL SUBROUTINE DFEQ TO CALCULATE EACH CASE
YIELD.....
        call dfeq(tau1,ae1,be1,yield,9001)
        ye1=15./21.*yield
        call dfeq(tau1,ad1,bd1,yield,9001)
        yd1=6./21.*yield
        call dfeq(tau2,ae2,be2,yield,9001)
        ye2=15./21.*ece1*yield
        call dfeq(tau2,ad2,bd2,yield,9001)
        yd2=6.0/21.*ecd1*yield
        yldf=ye1+yd1+ye2+yd2
        return
        end
```

```
C-----------------------------------------------------------
C
C       Subroutine to Calculate Glucose
C       in Reactor 1
C-----------------------------------------------------------
        function fyr1(tau,rho,be,temp1,temp2,conc,w)

        t1=temp1
        t2=temp2
        c=conc
C
C       .....CALCULATE THE COEFFICENTS.....
        ae1=ak3(t1,c)/ak1(t1,c)
        ad1=ak3(t1,c)/ak2(t1,c)
        ae2=ak3(t2,c)/ak1(t2,c)
        ad2=ak3(t2,c)/ak2(t2,c)
        be1=be
        bd1=be1*ak2(t1,c)/ak1(t1,c)
        be2=be1*ak1(t2,c)/ak1(t1,c)/w
        bd2=be1*ak2(t2,c)/ak1(t1,c)/w
        ue1=ae1*be1
        ud1=ad1*bd1
        tau1=tau*rho
        tau2=tau*(1.-rho)
        ce1=be1*tau1
        cd1=bd1*tau1
        if(ce1.gt.50.) then
        ece1=0.0
        elseif(tau1.eq.0.0) then
        ece1=1.0
        else
        ece1=exp(-ce1)
        endif
        if(cd1.gt.50.) then
        ecd1=0.0
        elseif(tau1.eq.0.0) then
        ecd1=1.0
        else
        ecd1=exp(-cd1)
        endif
C       .....CALL SUBROUTINE DFEQ TO CALCULATE EACH CASE
YIELD.....
        call dfeq(tau1,ae1,be1,yield,9001)
        ye1=15./21.*yield
        call dfeq(tau1,ad1,bd1,yield,9001)
        yd1=6./21.*yield
        fyr1=ye1+yd1
C       print *, "yldf=", yldf
        return
        end
```

```
C------------------------------------------------------------
C
C       Subroutine to Calculate Yield
C
C------------------------------------------------------------
        function  gyldf(tau,rho,be,temp1,temp2,conc,w)
        t1=temp1
        t2=temp2
        c=conc
        a1=ak5(t1,c)/ak4(t1,c)
        a2=ak5(t2,c)/ak4(t2,c)
        b1=be*ak4(t1,c)/ak1(t1,c)
        b2=be*ak4(t2,c)/ak1(t1,c)/w
        tau1=tau*rho
        tau2=tau*(1.0-rho)
        c1=b1*tau1
        print*,"a1=",a1,"b2=",b2
        if(c1.gt.50.)then
        ec1=0.0
        elseif(tau1.eq.0.)then
        ec1=1.0
        else
        ec1=exp(-c1)
        endif
        call dfeq(tau1,a1,b1,yield,9001)
        y1=yield
        call dfeq(tau2,a2,b2,yield,9001)
        y2=ec1*yield
        gyldf=y1+y2
        return
        end
```

```fortran
C-------------------------------------------------------------
C
C       Subroutine to Calculate Glucose
C       in Reactor 2
C-------------------------------------------------------------
        function fyr2(tau,rho,be,temp1,temp2,conc,w)
        t1=temp1
        t2=temp2
        c=conc
C
C       .....CALCULATE THE COEFFICENTS.....
        ae1=ak3(t1,c)/ak1(t1,c)
        ad1=ak3(t1,c)/ak2(t1,c)
        ae2=ak3(t2,c)/ak1(t2,c)
        ad2=ak3(t2,c)/ak2(t2,c)
        be1=be
        bd1=be1*ak2(t1,c)/ak1(t1,c)
        be2=be1*ak1(t2,c)/ak1(t1,c)/w
        bd2=be1*ak2(t2,c)/ak1(t1,c)/w
        ue1=ae1*be1
        ud1=ad1*bd1
        tau1=tau*rho
        tau2=tau*(1.-rho)
        ce1=be1*tau1
        cd1=bd1*tau1
        if(ce1.gt.50.) then
        ece1=0.0
        elseif(tau1.eq.0.0) then
        ece1=1.0
        else
        ece1=exp(-ce1)
        endif
        if(cd1.gt.50.) then
        ecd1=0.0
        elseif(tau1.eq.0.0) then
        ecd1=1.0
        else
        ecd1=exp(-cd1)
        endif
C
C       .....CALL SUBROUTINE DFEQ TO CALCULATE EACH CASE YIELD...
        call dfeq(tau2,ae2,be2,yield,9001)
        ye2=15./21.*ece1*yield
        call dfeq(tau2,ad2,bd2,yield,9001)
        yd2=6.0/21.*ecd1*yield
        fyr2=ye2+yd2
        return
        end
C-------------------------------------------------------------
C
```

```fortran
C       Subroutine to Calculate Difference Equation
C
C-------------------------------------------------------------
        subroutine dfeq(tau,alpha, beta, yield,N)
        dimension sol(9001,101)
C       goto 911
        if(tau.eq.0.0)then
        yield=0.0
        goto 999
        endif
        upper=1000.*tau + 1001.
        kupper=ifix(upper)
C
C       ..... GIVE INITIAL AND BOUNDARY CONDITIONS.....
        do 10 i=1,kupper
        sol(i,1)=0.0
   10   continue
        do 11 j=2,101
        sol(1,j)=0.0
   11   continue
C
C       .....CALCULATE SOLUTION BY ADDING EACH TERM.....
        delt=0.001
        delz=0.01
        do 100 i=2,kupper
        do 110 j=2,101
        tnm1=delt*(float(i)-2.)
        zim1=delz*(float(j)-2.)
        s1=(1.0-delt/delz-alpha*beta*delt)*sol(i-1,j)
        s2=delt/delz*sol(i-1,j-1)
        if(tnm1.gt.zim1)then
        atm=tnm1-zim1
        else
        atm=0.0
        endif
        s3=beta*delt*exp(-beta*atm)
        sol(i,j)=s1+s2+s3
  110   continue
  100   continue
C       .....INTEGRATE NUMERICALLY.....
        sum=0.0
        do 200 k=1001,kupper
        sum= sum + sol(k,101)
  200   continue
        yield=delt*sum
C       print *, yield
  999   return
        end
```

```
C------------------------------------------------------------
C
C       Subroutine to Seek the Maximum Yield
C       in Uniform Temperature
C
C------------------------------------------------------------
        subroutine seek1(array,bta,amax,lim)
C
C SUBROUTINE SEEK1 FOR THE MAXIMUM VALUE AND BETA  VALUE
        dimension array(500)
        bta=0.1
        amax=array(1)
        do 6 i=2,lim
        if(array(i) .gt. amax) then
        amax=array(i)
        bta=float(i+1)/10.
        endif
    6   continue
        return
        end
C------------------------------------------------------------
C
C       Subroutine to Seek Maximum Yield
C       in Temperature Step Change
C
C------------------------------------------------------------
        subroutine seek2(array,mth,tmax,lim)
        dimension array(60)
        tmax=array(1)
        mth=1
        do 10 i=2, lim
        if (array(i).gt.tmax) then
           tmax=array(i)
           mth=i
        endif
   10   continue
        return
        end
```

```
C------------------------------------------------------------
C
C        Subroutine to Calculate Rate Constants, K1
C------------------------------------------------------------
C
         function ak1(temp,conc)
         r=1.987
         t=temp+273.15
         c=conc
         ak1=6.17*(10.**13.)*(c**1.40)*exp(-28000./r/t)
         return
         end
C------------------------------------------------------------
C
C        Subroutine to Calculate Rate Constant, K2
C------------------------------------------------------------
         function ak2(temp,conc)
         r=1.987
         t=temp+273.15
         c=conc
         ak2=1.88*(10.**14.)*(c**1.20)*exp(-31000./r/t)
         return
         end
C------------------------------------------------------------
C
C        Subroutine to Calculate Rate Constant, K3
C------------------------------------------------------------
         function ak3(temp,conc)
         r=1.987
         t=temp+273.15
         c=conc
         ak3=1.01*(10.**11.)*(c**0.48)*exp(-25330./r/t)
         return
         end
```

```
C----------------------------------------------------------
C
C       Subroutine to Calculate Rate Constant, K4
C----------------------------------------------------------
        function ak4(temp,conc)
        r=1.987
        t=temp+273.15
        c=conc
        ak4=0.44*(10.**19.)*c*exp(-42900./r/t)
        return
        end
C----------------------------------------------------------
C
C       Subroutine to Calculate Rate Constant, K5
C----------------------------------------------------------
        function ak5(temp,conc)
        r=1.987
        t=temp+273.15
        c=conc
        ak5=0.28*(10.**14.)*(c**1.8)*exp(-30000./r/t)
        return
        end
```

```
C------------------------------------------------------------
C
C       Subroutine to Calculate Hemicellulose Remaining
C       in Reactor 1
C------------------------------------------------------------
        subroutine hemic1(t1,c,tm1,hcl)
        bk1=ak1(t1,c)
        bk2=ak2(t1,c)
        xlf=exp(-bk1*tm1)
        xls=exp(-bk2*tm1)
        hcr=1.0-15./21.*xlf-6./21.*xls
        hcl=hcr*100.
        return
        end
C------------------------------------------------------------
C
C       Subroutine to Calculate Hemicellulose Remainin
C       in Reactor 2
C------------------------------------------------------------
        subroutine hemic2(t1,t2,c,tm1,tm2,hcl2)
        hf1=ak1(t1,c)
        hs1=ak2(t1,c)
        hf2=ak1(t2,c)
        hs2=ak2(t2,c)
        xf1=exp(-hf1*tm1)
        xs1=exp(-hs1*tm1)
        xf2=exp(-hf2*tm2)
        xs2=exp(-hs2*tm2)
        hr=1.0-(15./21.*xf1+6./21*xs1)*(15./21.*xf2+6./21.*xs2)
        hcl2=hr*100.
        return
        end
```

```
C------------------------------------------------------------
C
C       Subroutine to Calculate Cellulose Remaining
C       in Reactor 1
C------------------------------------------------------------
        subroutine cellr1(t1,c,tm1,cl)
        bk4=ak4(t1,c)
        xl=exp(-bk4*tm1)
        cr=1.0-xl
        cl=cr*100.
        return
        end
C------------------------------------------------------------
C
C       Subroutine to Calculate Cellulose Remaining
C       in Reactor 2
C------------------------------------------------------------
        subroutine cellr(t1,t2,c,tm1,tm2,cl)
        bk4l=ak4(t1,c)
        bk4h=ak4(t2,c)
        xl=exp(-bk4l*tm1)
        xh=exp(-bk4h*tm2)
        cr=1.0-xl*xh
        cl=cr*100.
        return
        end
C
C
```

```
C------------------------------------------------------------
C
C       Subroutine to Determine Optimal Linear Velocity
C
C------------------------------------------------------------
        subroutine rxncon1(rlen,tau,beta,t1,c,tm,vel,qv,a)
        x=beta/ak1(t1,c)
        tm=x*tau
        vel=rlen/x
        qv=vel*a
        return
        end
C------------------------------------------------------------
C
C       Subroutine to Determine Optimal Volumetric Flow Rate
C
C------------------------------------------------------------
      subroutine rxncon(rlen,tau,beta,rho,t1,c,w,tm1, tm2, vel1,vel2,q1,q2,a)
        x=beta/ak1(t1,c)
        tau1=tau*rho
        tau2=tau*(1.0-rho)
        tm1=x*rho*tau
        tm2=x*(1.0-rho)*tau/w
        vel1=ak1(t1,c)*rlen/beta
        vel2=vel1*w
        q1=vel1*a
        q2=vel2*a
        return
        end
```

```
C------------------------------------------------------------
C      SUBROUTINE TO CALCULATE XYLOSE CONCENTRATION
C      AFTER RECYCLE
C
C------------------------------------------------------------
       subroutine recycle(t1,c,u,rho,rlen,yh,yl,ch,cl,fy,fc)
       decomp=exp(-ak3(t1,c)*rlen/u*1.0)
       if(rho.lt.0.5)then
       fy=yl+yh*(1-2.0*rho)/(1.0-rho)+yh*rho/(1.0-rho)*decomp
       fc=(1.0-2.0*rho)*ch+2.0*rho*(cl+ch*decomp)
       elseif(rho.eq.0.5)then
       fy=yl+yh*decomp
       fc=cl+ch*decomp
       else
       fy=yl+yh*decomp
       fc=((2.0*rho-1.0)*cl+(1.0-rho)*(cl+ch*decomp))/rho
       endif
       return
       end
```

```
C-------------------------------------------------------------
C
C      SUBROUTINE TO PRINT OUT 'XYLOSE YIELD', 'DECOMPOSED'
C      & 'HEMICELLULOSE UNREACTED'
C-------------------------------------------------------------
C
       subroutine output1(xly,dxl,xhy,dxh,xy,cy,dxlh)
       dimension xly(10),dxl(10),xhy(10),dxh(10),xy(10)
       dimension cy(10),dxlh(10)
       write(8,100)
       write(8,110)
       write(8,210)
       write(8,310)
       do 11 k=1,5
       h1=100.-xly(k)-dxl(k)
       h2=100.-xhy(k)-dxh(k)
       h3=100.-xy(k)-dxlh(k)
       write(8,400)k,xly(k),dxl(k),h1,xhy(k),dxh(k),h2,xy(k),
      $cy(k),dxlh(k),h3
  11 continue
       write(8,510)
 100 format(t10,'-----RESULTS-----'/)
 110 format(t1,'#1 XYLOSE YIELD(%), DECOMPOSED(%)',
      +'& HEMICELLULOSE UNREACTED(%)',/,t1,79(1h-))
 210 format(t12'UNI LOW't33,'UNI HIGH',t55,'STEP CHANGE'
      $,/,t1'TAU',t7,'YIELD',t14,'DECOMP', t21,' HC'
      $,t28, 'YIELD',t35,'DECOMP', t42,'HC',t49,'YIELD',t57,
      $'CONC. ',t63,'DECOMP',t70,'HC')
 310 format(t1,79(1h-))
 400 format(1x,i2,2x,10(f6.2,x))
 510 format(1x,79(1h-),/)
       return
       end
```

```
C-----------------------------------------------------------
C
C     SUBROUTINE TO PRINT OUT 'CELLULOSE HYDROLYZED' &
C     "GLUCOSE DECOMPOSED"
C-----------------------------------------------------------
C
      subroutine output2(dcllo,dgl,dclhi,dgh,dcl,dglh)
      dimension dcllo(10),dclhi(10),dcl(10)
      dimension  dgl(10),dgh(10),dglh(10)
      write(8,110)
      write(8,200)
      write(8,210)
      write(8,310)
      do 10 k=1,5
      write(8,400) k,dcllo(k),dgl(k),dclhi(k),dgh(k),dcl(k),
      dglh(k)
   10 continue
      write(8,510)
  110 format(t1,'#2 CELLULOSE HYDROLYZED(%) & GLUCOSE
     $DECOMPOSED', '(%)',/,t1,79(1h-))
  200 format(t13,'UNI LOW',t33,'UNI HIGH',t53,'STEP CHANGE')
  210 format(t1,'TAU',t9,'C.H.',t19,'G.D.',t29,'C.H.',t39,
     $'G.D.',t49,'C.H.',t59,'G.D.')
  310 format(t1,79(1h-))
  400 format(1x,i2,x,6(f9.3,x))
  510 format(1x,79(1h-),/)
      return
      end
```

```
C-------------------------------------------------------------
C
C     SUBROUTINE TO PRINT OUT "OPTIMAL REACTION TIME" &
C     "VOLUMETRIC FLOW RATE"
C-------------------------------------------------------------
C
      subrutine output4(tml,vell,tmh,velh,tm1,tm2,vel1,vel2)
      dimension tml(10),vell(10),tmh(10),velh(10)
      dimension tm1(10),tm2(10),vel1(10),vel2(10)
      write(8,110)
      write(8,200)
      write(8,210)
      write(8,310)
      do 11 k=1,5
      write(8,400)k,tml(k),vell(k),tmh(k),velh(k),tm1(k),
      tm2(k),vel1(k),vel2(k)
   11 continue
      write(8,510)
  110 format(t1,'#3 OPTIMAL RXN TIME(MINS)& VOLUMETRIC FLOW
     $RATE','(CC/MINS)',/,t1,79(1h-))
  200 format(t9,'UNI LOW',t25,'UNI HIGH',t45,'STEP CHANGE')
  210 format(t1,'TAU',t8,'R.T.',t16,'VFR',t24,'R.T.',t32,
     $'VFR', t40,'RT1.',t48,'RT2.',t56,'VFR1',t64,'VFR2')
  310 format(t1,79(1h-))
  400 format(1x,i2,2x,8(f7.3,x))
  510 format(1x,79(1h-),/)
      return
      end
```

```
C--------------------------------------------------------------
C
C    SUBROUTINE TO PRINT OUT "FINAL PRODUCT CONCENTRATION" &
C    PRODUCT YIELD IN THE REVERSE FLOW CONFIGURATION
C--------------------------------------------------------------
C
      subroutine output5(dfy,dfc,rho,obeta)
      dimension dfy(10),dfc(10),rho(10),obeta(10)
      write(8,110)
      write(8,210)
      write(8,310)
      do 11 k=1,5
      write(8,400) k,dfc(k),dfy(k),rho(k),obeta(k)
   11 continue
      write(8,510)
  110 format(t1,'#4 FINAL PRODUCT CONC.(%) & PRODUCT YIELD',
     $'(%) WITH REVERSE STREAM'/,t1,79(1h-))
  210 format(t1,'TAU',t9,'PRODUCT CONC.',t25,'PRODUCT YIELD'
     $,t41,'RHO',t56,'OPTIMAL BETA')
  310 format(t1,79(1h-))
  400 format(1x,i2,2x,4(f10.3,6x))
  510 format(1x,79(1h-),/)
      return
      end
```

APPENDIX E

TASK II: SWITCHGRASS KINETIC STUDY

Figure 1. Decay of Xylan Content in Hemicellulose during hydrolysis
(Temperature = 120 c, Solid / Liquid = 1:10.4)
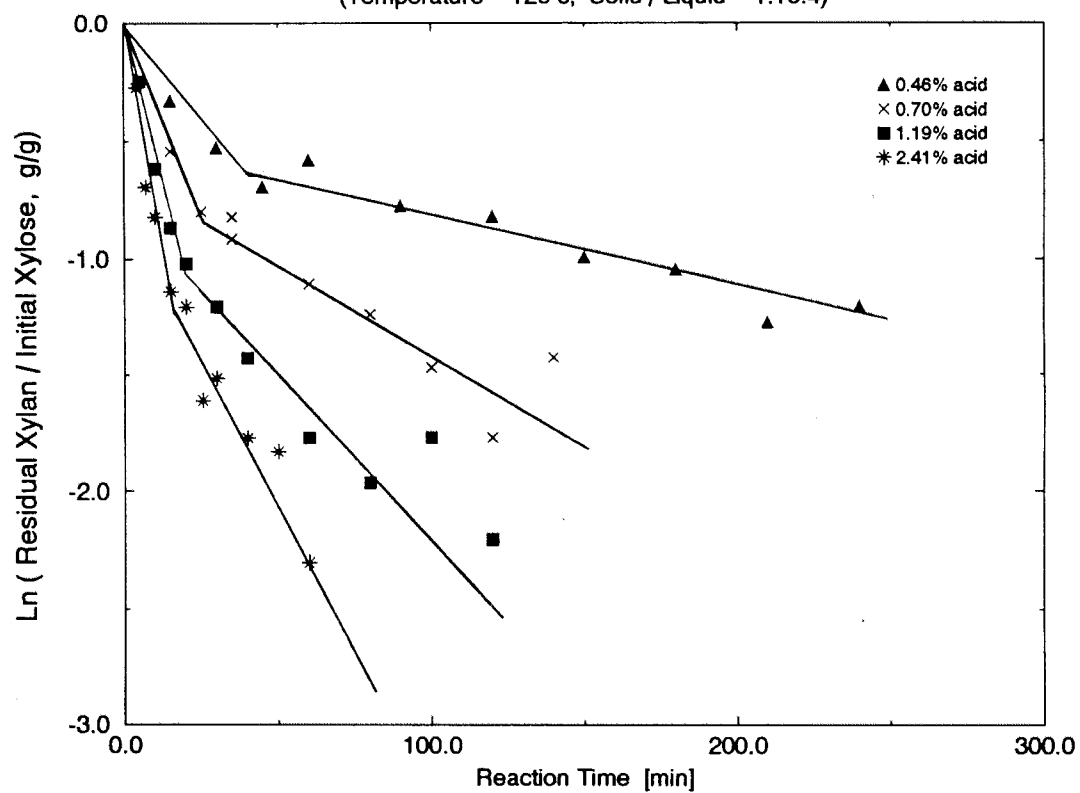
Table 1. Kinetic Parameters from Modelling[a]

Temperature ($^\circ$C)	k_1 [min^{-1}(%w/w)$^{-1.2}$]	k_2 [min^{-1}(%w/w)$^{-1.2}$]	k_3 [min^{-1}(%w/w)$^{-1.6}$]	k_4[b] [min^{-1}(%w/w)]
120	0.0902	0.00563	0.0341	0.000226
130	0.1720	0.01133	0.0792	0.000550
135	0.1968	0.01716	0.1007	0.000845
140	0.2479	0.02485	0.1888	0.001280

a: F_f=0.65; n_1, n_2 and n_3 = 1.2, 1.2 and 1.6 respectively.
b: The k_4 data were taken from the work of Kim and Lee, Biotechnol. and Bioeng., Symp. No.17, 71-84, 1986.

Table 2. Activation Energy for Each Reactions

k_i	k_{oi} [min^{-1}(%w/w)$^{-n_i}$]	n_i	E_i[kcal/g mol]
1	$9.225*10^7$	1.20	16.2
2	$1.192*10^{11}$	1.20	24.0
3	$1.675*10^{13}$	1.60	26.4
4	$1.010*10^{11}$	0.48	25.3

Figure 2. Arrhenius Equations for Switchgrass Hydrolysis
(solid/liquid = 1:10.4)
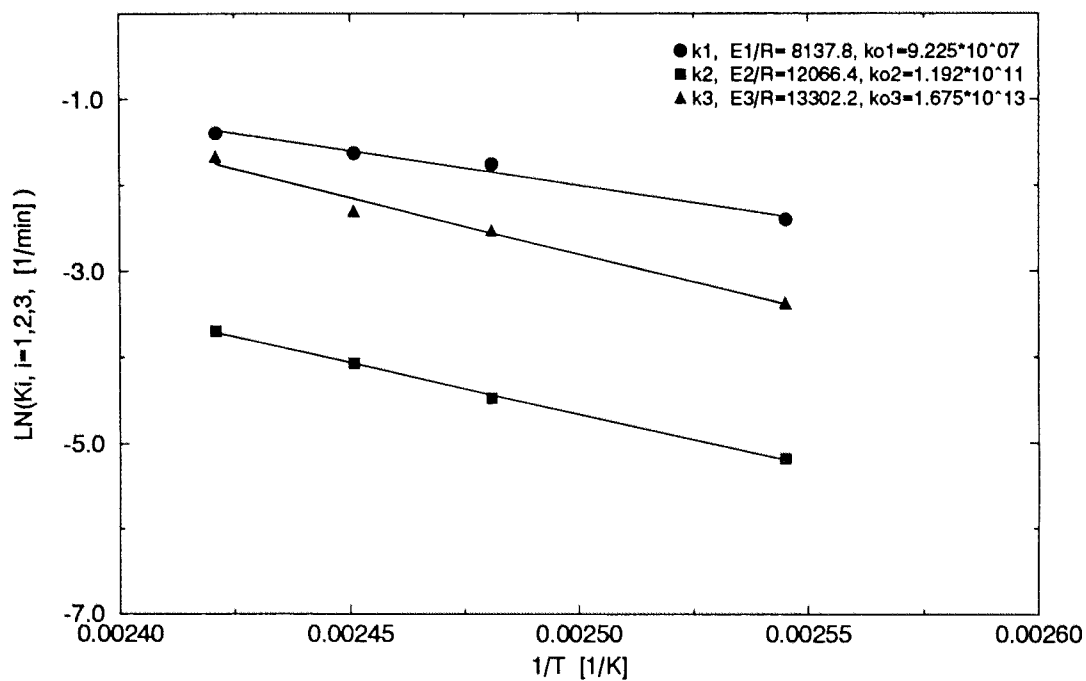
```
                   Non-Linear Least Squares Iterative Phase
                Dependent Variable Y    Method: Gauss-Newton
     Iter          KK1              KK2              KK3 Sum of Squares
        0        0.090000         0.005000         0.020000        12.370109
        1        0.102155         0.004365         0.034920         4.856595
        2        0.091163         0.005639         0.033621         4.331532
        3        0.090164         0.005626         0.034072         4.326511
NOTE: Convergence criterion met.
```

```
     Non-Linear Least Squares Summary Statistics      Dependent Variable Y

        Source                 DF Sum of Squares     Mean Square

        Regression              3    221.70162900     73.90054300
        Residual               47      4.32651056      0.09205342
        Uncorrected Total      50    226.02813956

        (Corrected Total)      49     74.40722779
```

```
     Parameter      Estimate      Asymptotic               Asymptotic 95 %
                                  Std. Error            Confidence Interval
                                                       Lower           Upper
        KK1    0.0901639997 0.00613167885 0.07782868635 0.10249931313
        KK2    0.0056261684 0.00071357128 0.00419065203 0.00706168477
        KK3    0.0340721428 0.00316574876 0.02770349496 0.04044079056
```

```
                   Asymptotic Correlation Matrix

     Corr                    KK1                 KK2                 KK3
     ----------------------------------------------------------------------
        KK1                    1        -0.388849457        0.2202379241
        KK2          -0.388849457                  1        -0.703589833
        KK3          0.2202379241        -0.703589833                  1
```

Non-Linear Least Squares Iterative Phase
Dependent Variable Y   Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.150000	0.013400	0.080000	5.305281
1	0.162757	0.011210	0.078770	4.507740
2	0.168940	0.011349	0.079058	4.453594
3	0.171105	0.011339	0.079176	4.446832
4	0.171756	0.011337	0.079196	4.445552
5	0.171943	0.011336	0.079199	4.445247
6	0.171995	0.011336	0.079200	4.445166
7	0.172010	0.011336	0.079200	4.445143
8	0.172014	0.011336	0.079200	4.445137

Non-Linear Least Squares Iterative Phase
Dependent Variable Y   Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
9	0.172015	0.011336	0.079200	4.445135
10	0.172016	0.011336	0.079200	4.445135
11	0.172016	0.011336	0.079200	4.445135
12	0.172016	0.011336	0.079200	4.445135
13	0.172016	0.011336	0.079200	4.445135
14	0.172016	0.011336	0.079200	4.445135
15	0.172016	0.011336	0.079200	4.445135
16	0.172016	0.011336	0.079200	4.445135
17	0.172016	0.011336	0.079200	4.445135

Non-Linear Least Squares Iterative Phase
Dependent Variable Y   Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
18	0.172016	0.011336	0.079200	4.445135

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics   Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	379.69346979	126.56448993
Residual	43	4.44513476	0.10337523
Uncorrected Total	46	384.13860455	
(Corrected Total)	45	102.88876112	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
KK1	0.1720158306	0.01183271818	0.14815296970	0.19587869159
KK2	0.0113361547	0.00094096511	0.00943852480	0.01323378458
KK3	0.0791997852	0.00751004283	0.06405439723	0.09434517319

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	-0.141905331	-0.056431808
KK2	-0.141905331	1	-0.62807398

Non-Linear Least Squares Iterative Phase
Dependent Variable Y   Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.190000	0.022000	0.070000	8.309720
1	0.204662	0.016644	0.091512	7.119970
2	0.196752	0.017163	0.100662	6.878778

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics   Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	310.33330588	103.44443529
Residual	44	6.87877842	0.15633587
Uncorrected Total	47	317.21208430	
(Corrected Total)	46	86.72315965	

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Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
KK1	0.1967520139	0.01302054048	0.17051093029	0.22299309757
KK2	0.0171633331	0.00212987289	0.01287087126	0.02145579485
KK3	0.1006620344	0.01200895005	0.07645967016	0.12486439858

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	-0.207257294	-0.072131359
KK2	-0.207257294	1	-0.678936175
KK3	-0.072131359	-0.678936175	1

Non-Linear Least Squares Iterative Phase
Dependent Variable Y   Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.230000	0.010000	0.130000	27.121374
1	0.241188	0.020239	0.200584	7.399802
2	0.254245	0.024580	0.172160	6.588193
3	0.246919	0.024846	0.184847	6.571163
4	0.247923	0.024849	0.188795	6.567595

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics   Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	335.99479138	111.99826379
Residual	44	6.56759467	0.14926352
Uncorrected Total	47	342.56238605	
(Corrected Total)	46	106.26230924	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
KK1	0.2479226168	0.00264691881	0.24258812103	0.25325711253
KK2	0.0248490377	0.00255087393	0.01970810699	0.02998996839
KK3	0.1887949394	0.02547446423	0.13745470909	0.24013516966

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	-0.048246504	0.1680782605
KK2	-0.048246504	1	-0.638336972
KK3	0.1680782605	-0.638336972	1

Appendix 2. Reaction Progression in Switchgrass Hydrolysis at 120c

(Acid Conc=0.46%, Solid:Liquid=1:10.4)
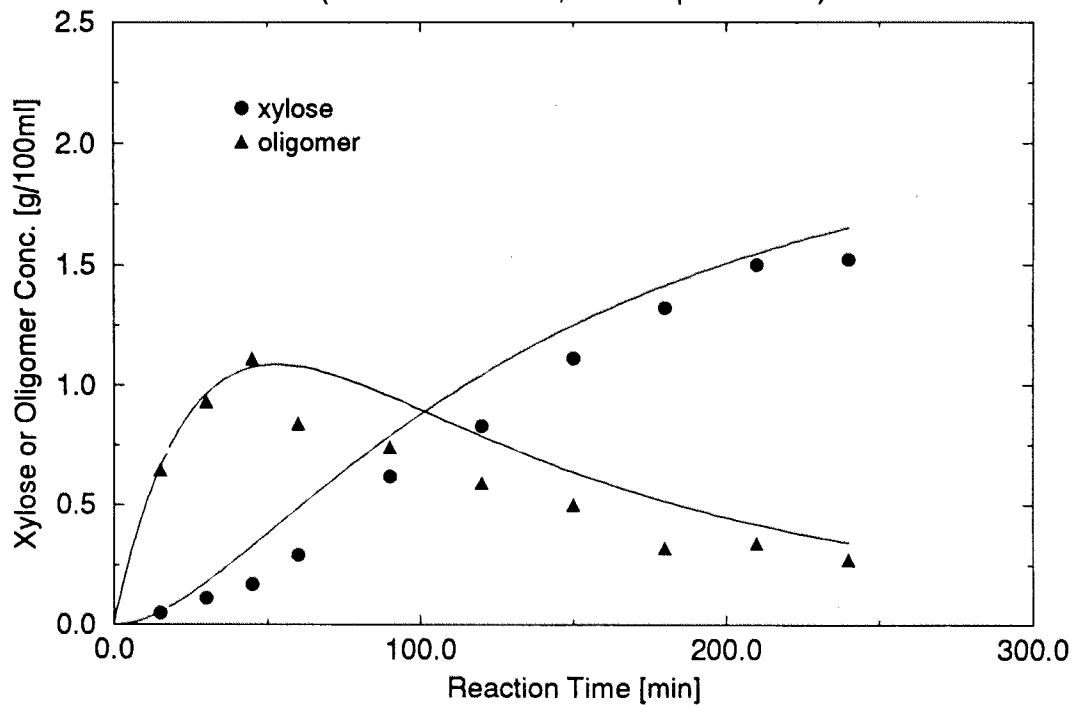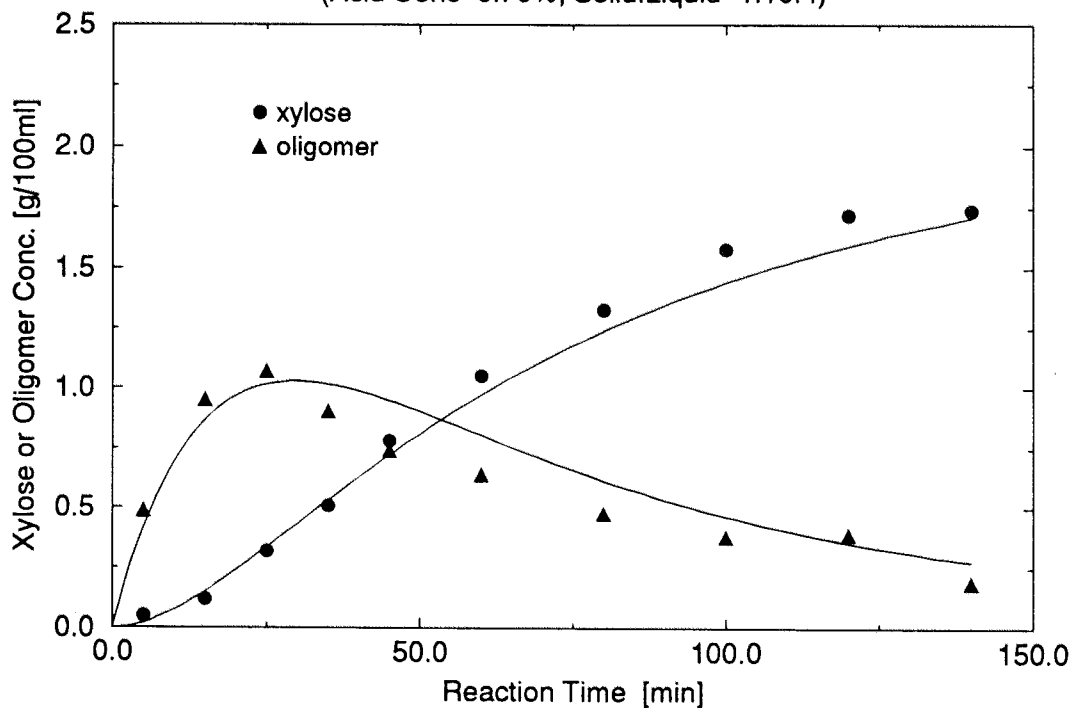
(Acid Conc=0.70%, Solid:Liquid=1:10.4)

(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 120c

(Acid Conc=1.19%, Solid:Liquid=1:10.4)
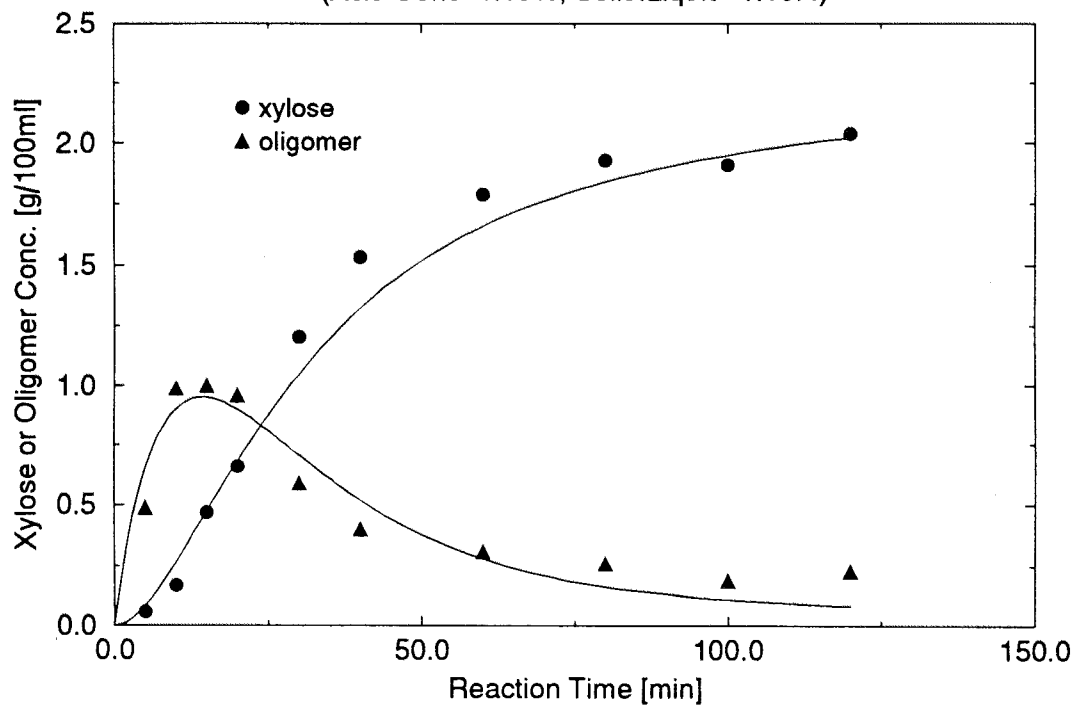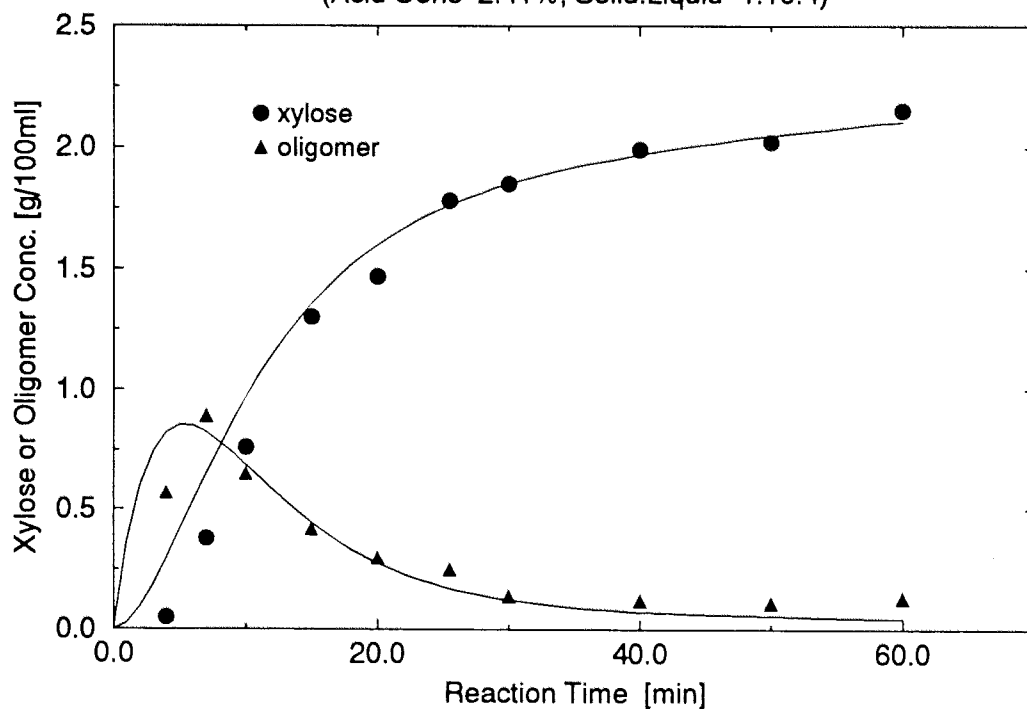
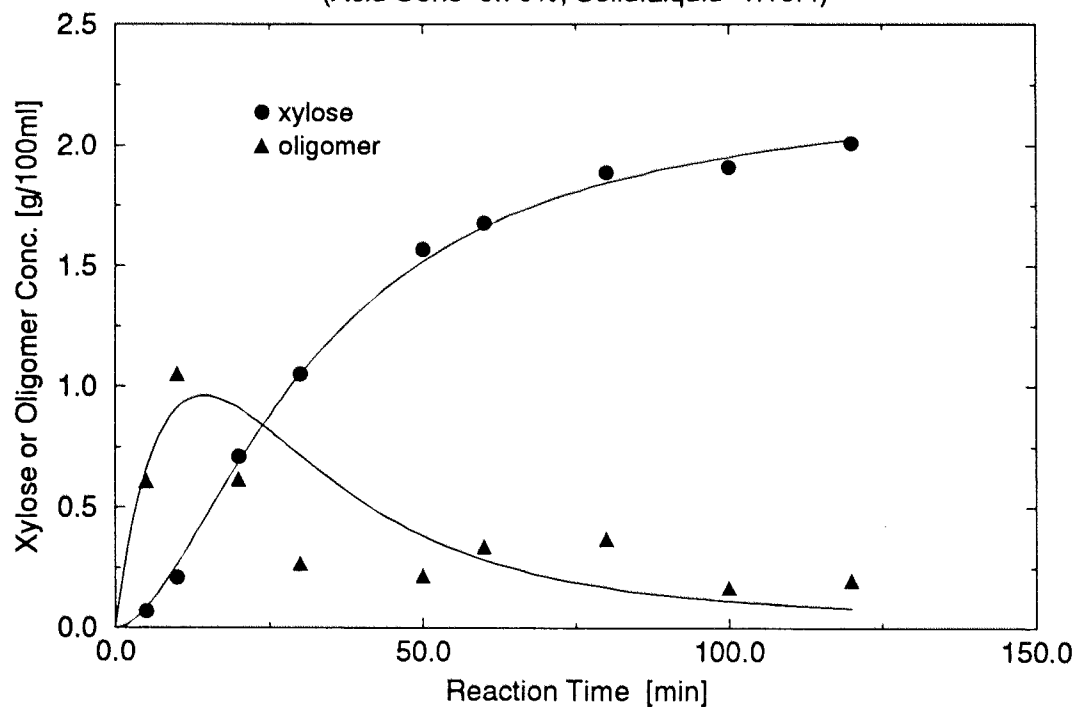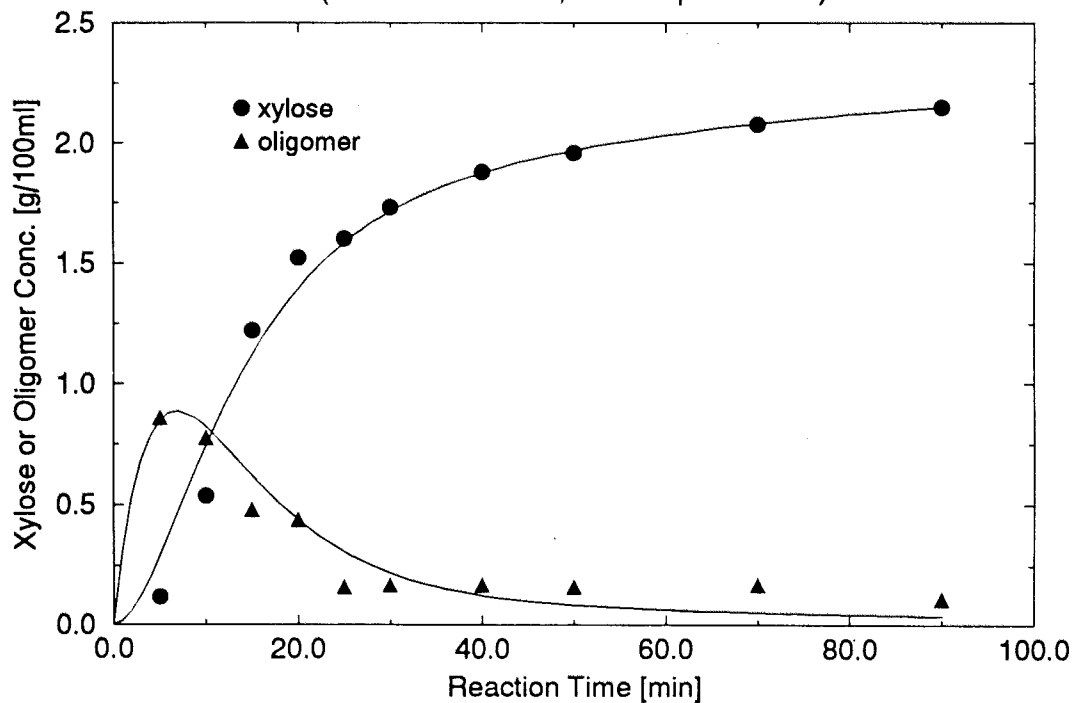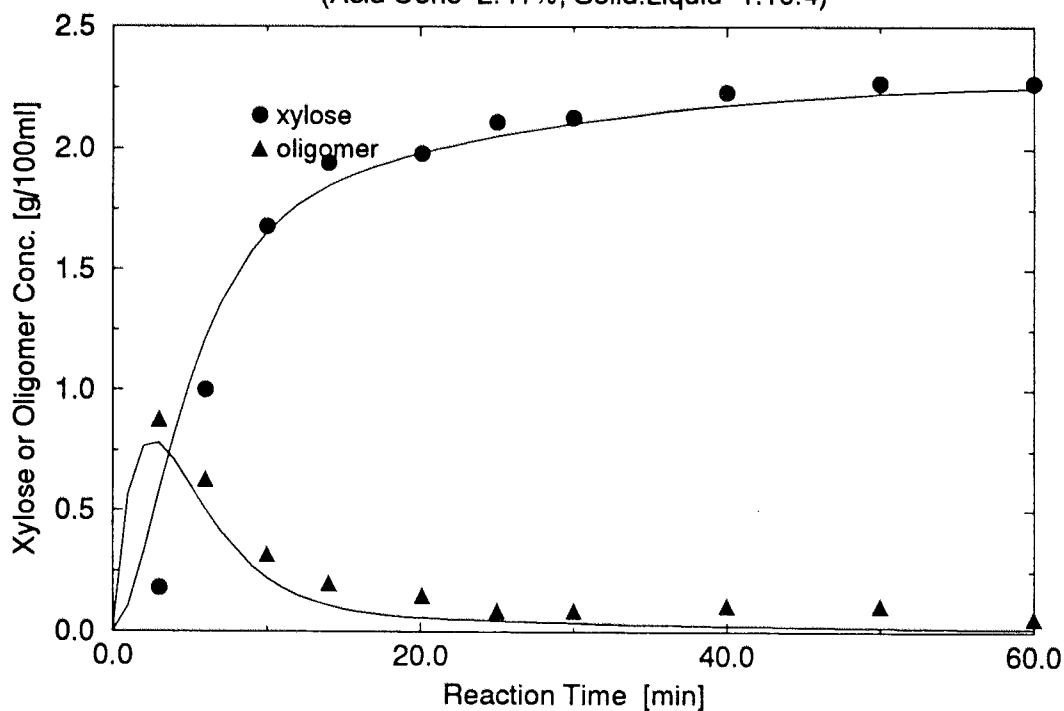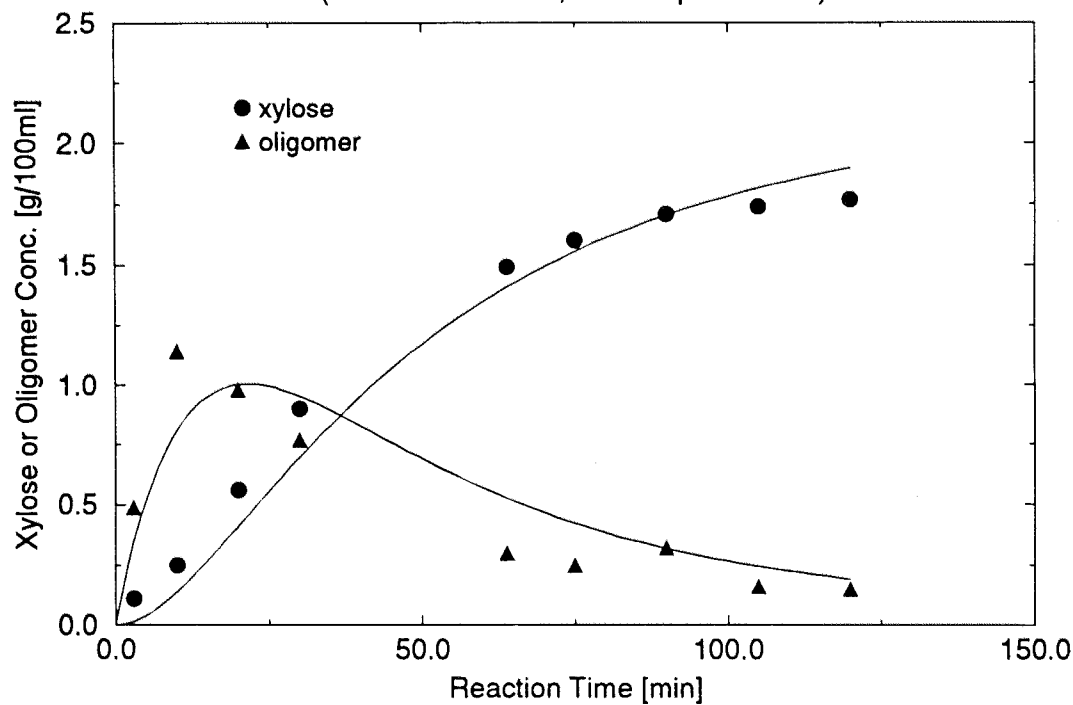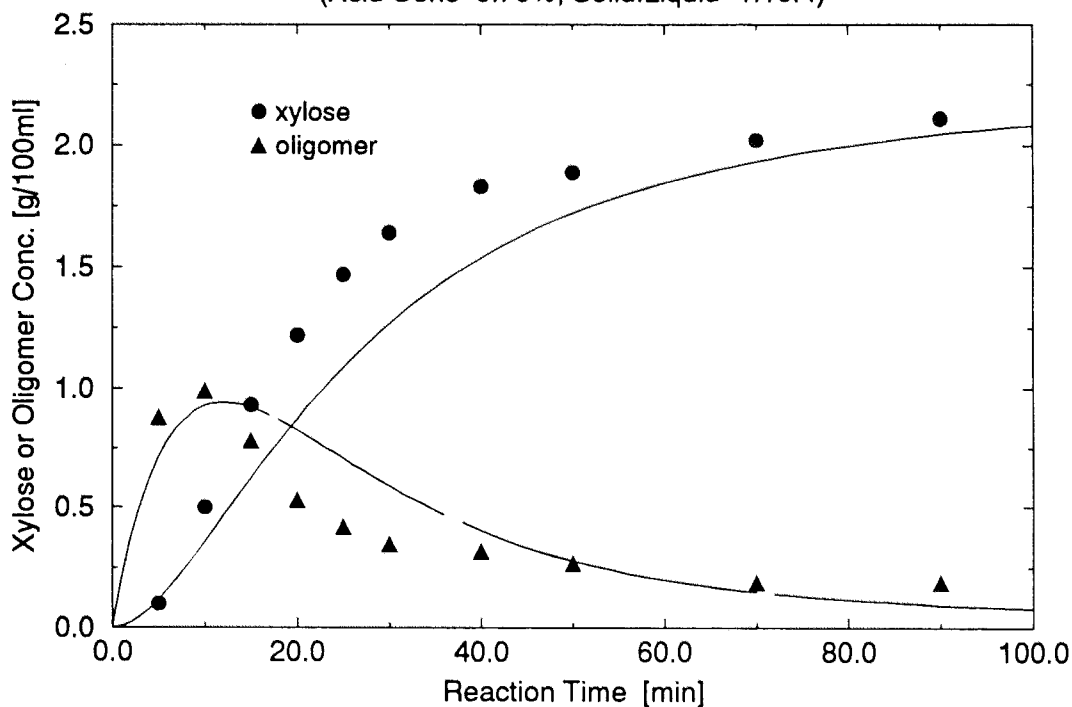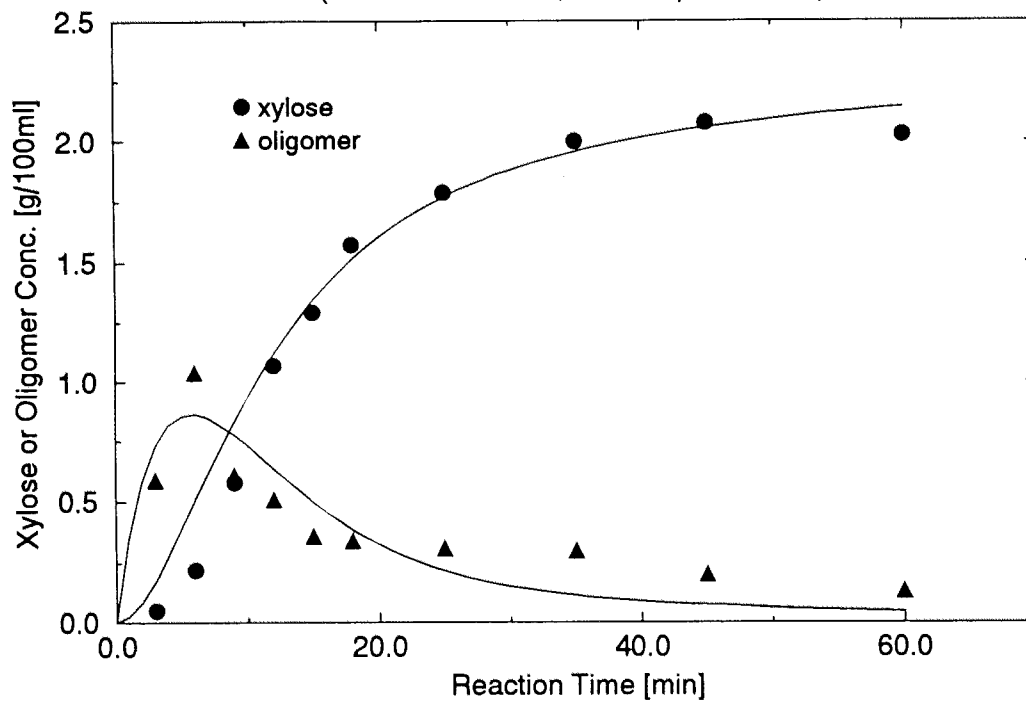## (Acid Conc=2.41%, Solid:Liquid=1:10.4)

(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 130c
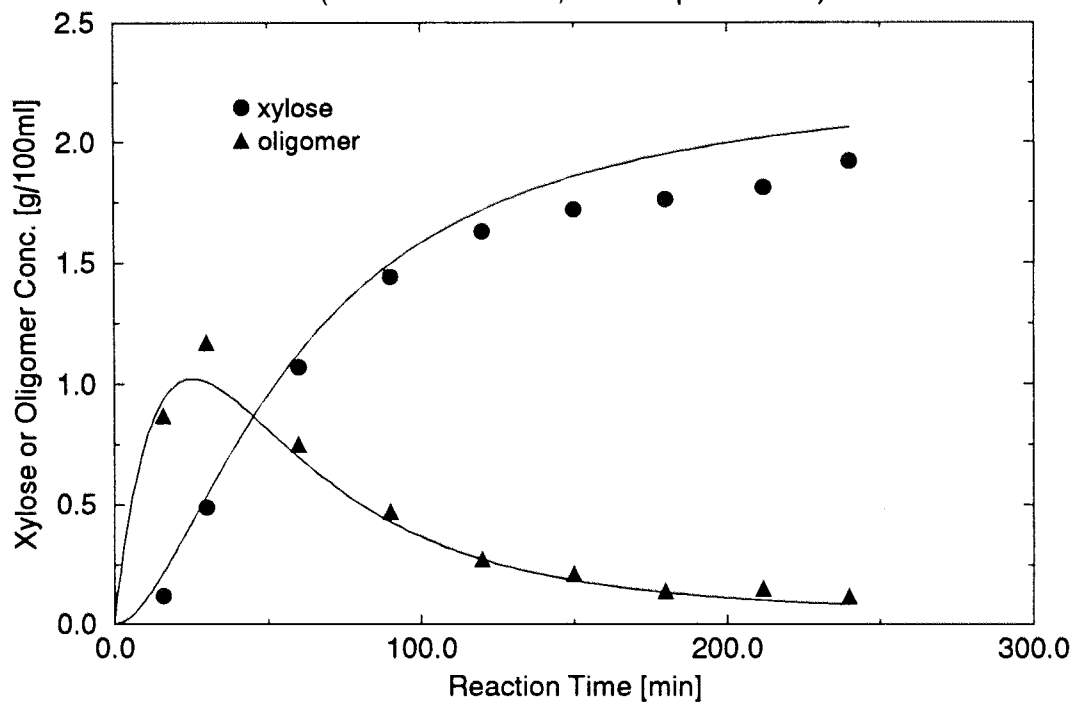
(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 130c

(--: Best Fit for Individual Run)

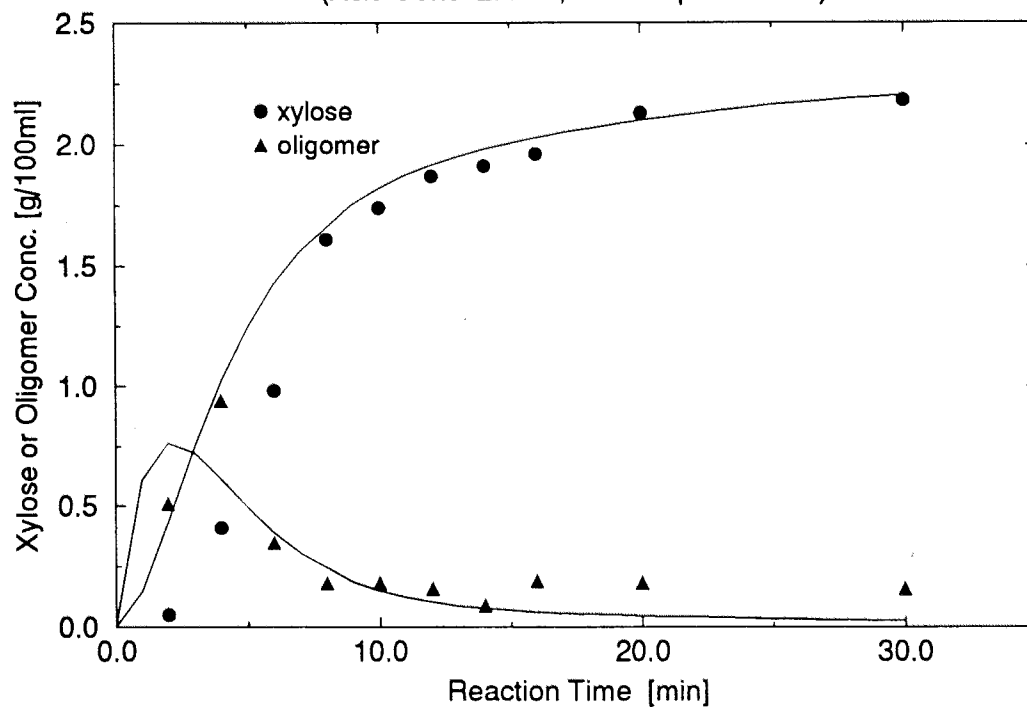# Reaction Progression in Switchgrass Hydrolysis at 135c

(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 135c
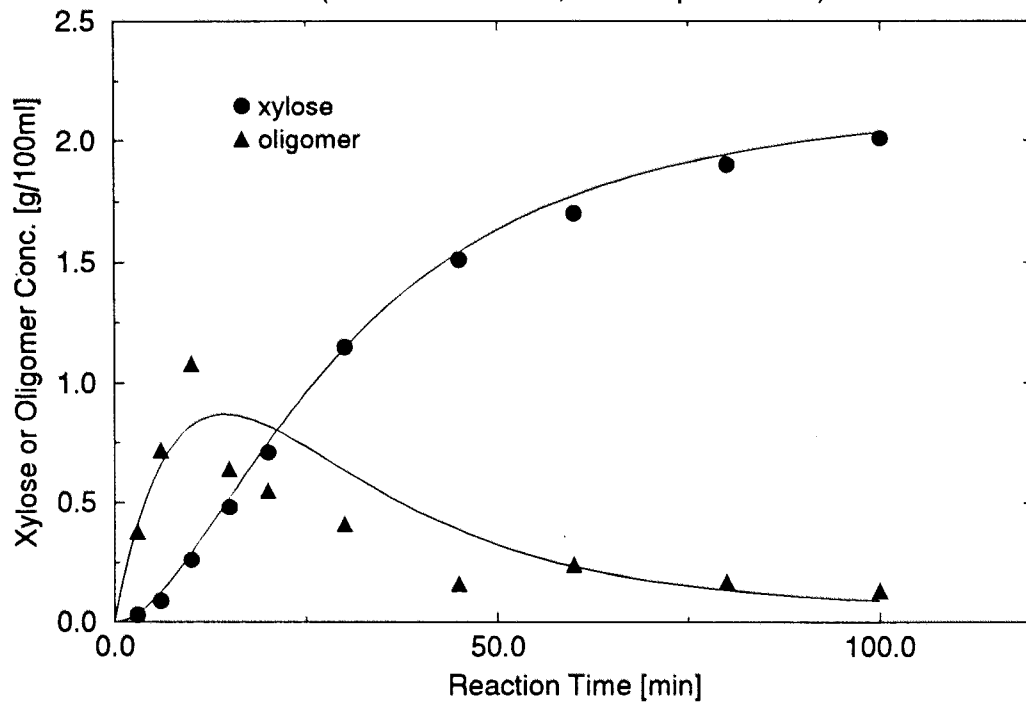

(Acid Conc=1.19%, Solid:Liquid=1:10.4)

(Acid Conc=2.41%, Solid:Liquid=1:10.4)

(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 140c

(Acid Conc=0.46%, Solid:Liquid=1:10.4)

(Acid Conc=0.70%, Solid:Liquid=1:10.4)

(--: Best Fit for Individual Run)

Reaction Progression in Switchgrass Hydrolysis at 140c

(Acid Conc=1.19%, Solid:Liquid=1:10.4)
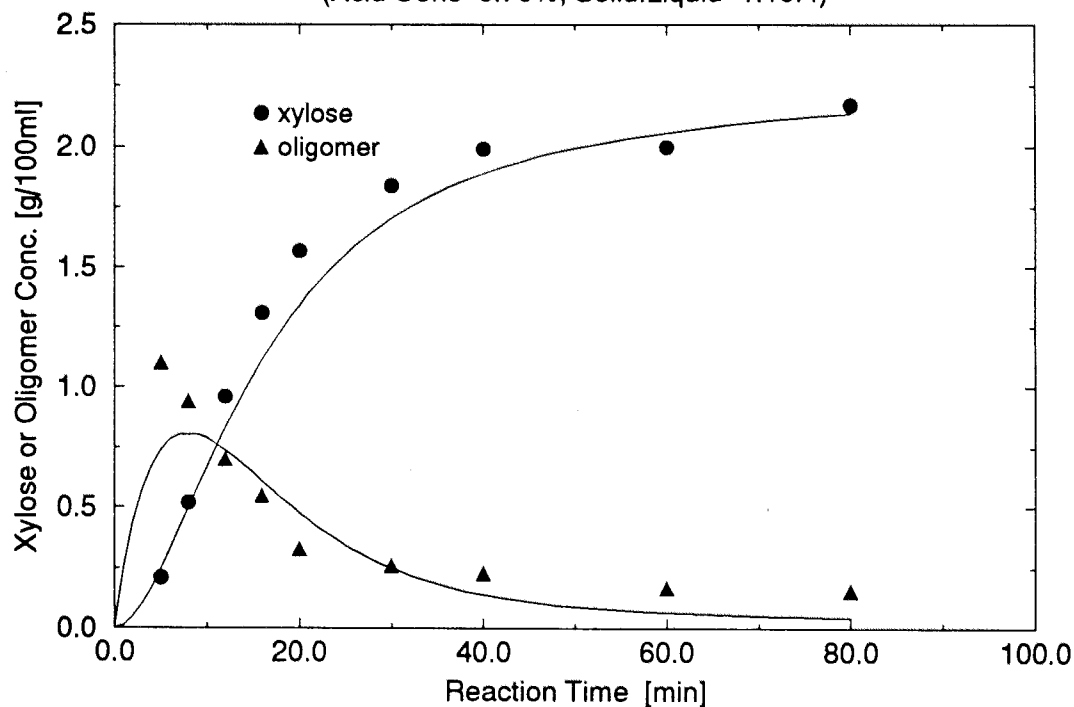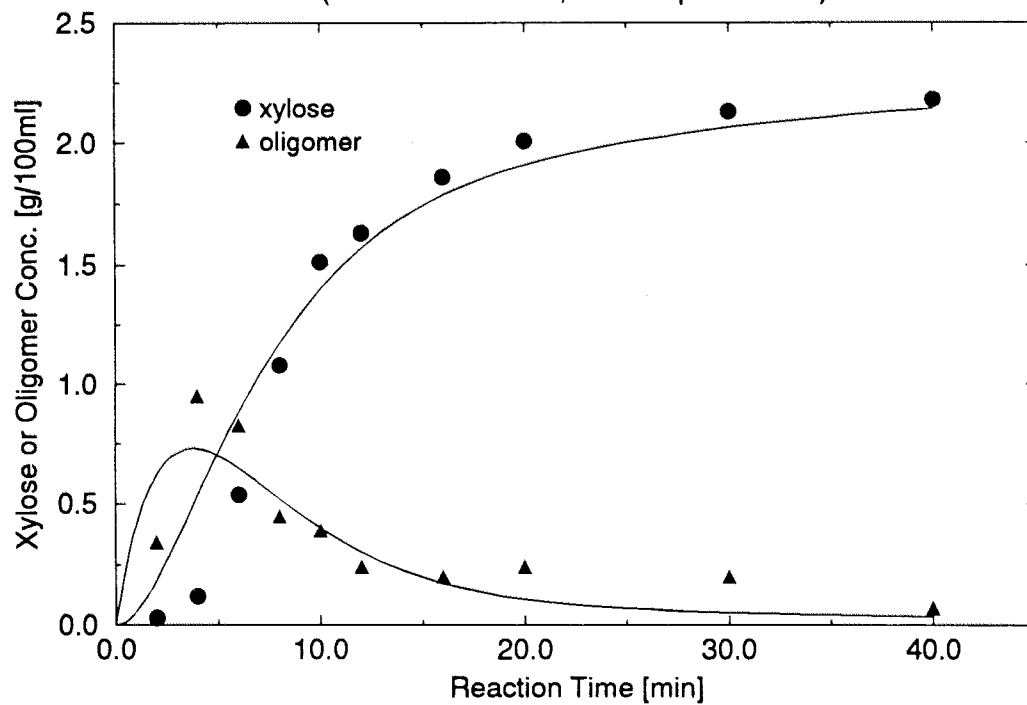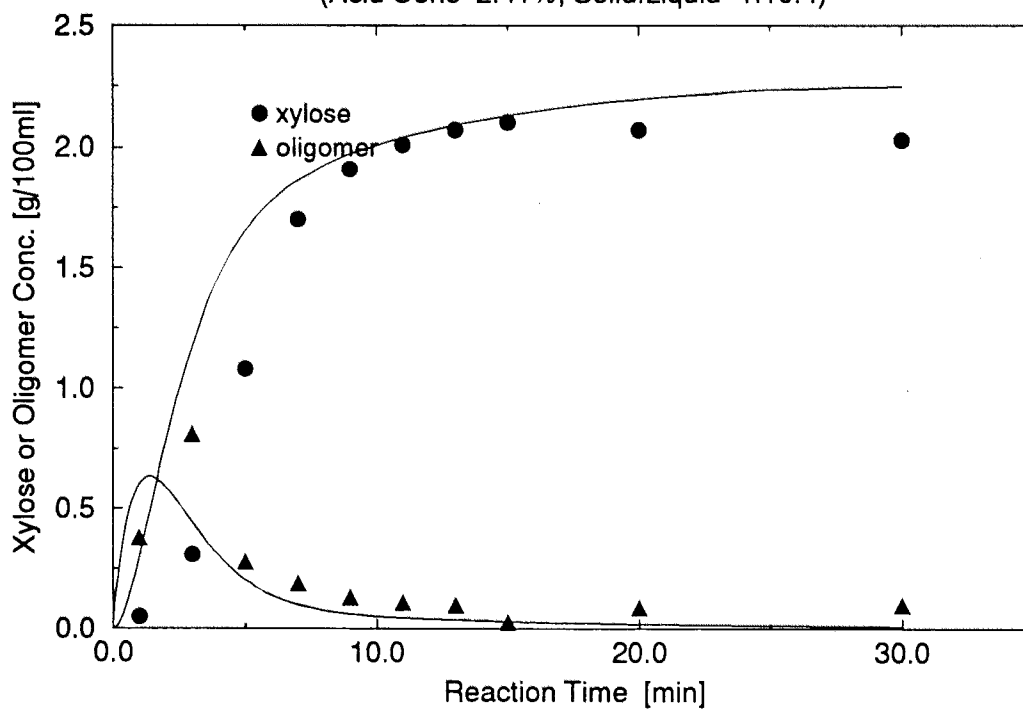
(Acid Conc=2.41%, Solid:Liquid=1:10.4)

(--: Best Fit for Individual Run)

APPENDIX F

TASK III: THERMAL DIFFUSIVITY DETERMINATION

Table 1. Thermal Diffusivity in Longitudinal Direction for Hybrid Poplar   67
                                   14:24 Thursday, September 16, 1993

Non-Linear Least Squares DUD Initialization   Dependent Variable THETA
                DUD   ALPHA Sum of Squares
                 -2   0.001000   35.806654
                 -1   0.001100   30.238870

             Non-Linear Least Squares Iterative Phase
              Dependent Variable THETA   Method: DUD
              Iter   ALPHA Sum of Squares
                 0   0.001100   30.238870
                 1   0.002119   3.971257
                 2   0.002654   0.751845
                 3   0.003009   0.179696
    Thermal Diffusivity in Longitudinal Direction for Hybrid Poplar   68
                                   14:24 Thursday, September 16, 1993

             Non-Linear Least Squares Iterative Phase
              Dependent Variable THETA   Method: DUD
              Iter   ALPHA Sum of Squares
                 4   0.003092   0.160250
                 5   0.003096   0.160228
                 6   0.003096   0.160228
NOTE: Convergence criterion met.

  Non-Linear Least Squares Summary Statistics   Dependent Variable THETA

     Source   DF Sum of Squares   Mean Square

     Regression   1   48.940305069   48.940305069
     Residual   243   0.160227575   0.000659373
     Uncorrected Total   244   49.100532644

     (Corrected Total)   243   24.963378536
     Thermal Diffusivity in Longitudinal Direction for Hybrid Poplar   69
                                   14:24 Thursday, September 16, 1993

     Parameter   Estimate   Asymptotic   Asymptotic 95 %
                                Std. Error   Confidence Interval
                                                     Lower   Upper
        ALPHA   0.0030963850 0.00001648241 0.00306391800 0.00312885207

                    Asymptotic Correlation Matrix

               Corr   ALPHA
               -
                    ALPHA   1

Table 2. Thermal Diffusivity in Radial Direction for Hybrid Poplar   70
                                         14:24 Thursday, September 16, 1993

    Non-Linear Least Squares DUD Initialization   Dependent Variable THETA
                    DUD   ALPHA Sum of Squares
                     -2   0.001000   14.006152
                     -1   0.001100   10.102859

                Non-Linear Least Squares Iterative Phase
                  Dependent Variable THETA   Method: DUD
                    Iter   ALPHA Sum of Squares
                      0   0.001100   10.102859
                      1   0.001625   0.959139
                      2   0.001799   0.370337
                      3   0.001858   0.329053
        Thermal Diffusivity in Radial Direction for Hybrid Poplar   71
                                         14:24 Thursday, September 16, 1993

                Non-Linear Least Squares Iterative Phase
                  Dependent Variable THETA   Method: DUD
                    Iter   ALPHA Sum of Squares
                      4   0.001864   0.328762
                      5   0.001864   0.328762
NOTE: Convergence criterion met.

    Non-Linear Least Squares Summary Statistics   Dependent Variable THETA

        Source   DF Sum of Squares   Mean Square

        Regression   1   74.562224778   74.562224778
        Residual   302   0.328762413   0.001088617
        Uncorrected Total   303   74.890987191

        (Corrected Total)   302   31.627640483
            Thermal Diffusivity in Radial Direction for Hybrid Poplar   72
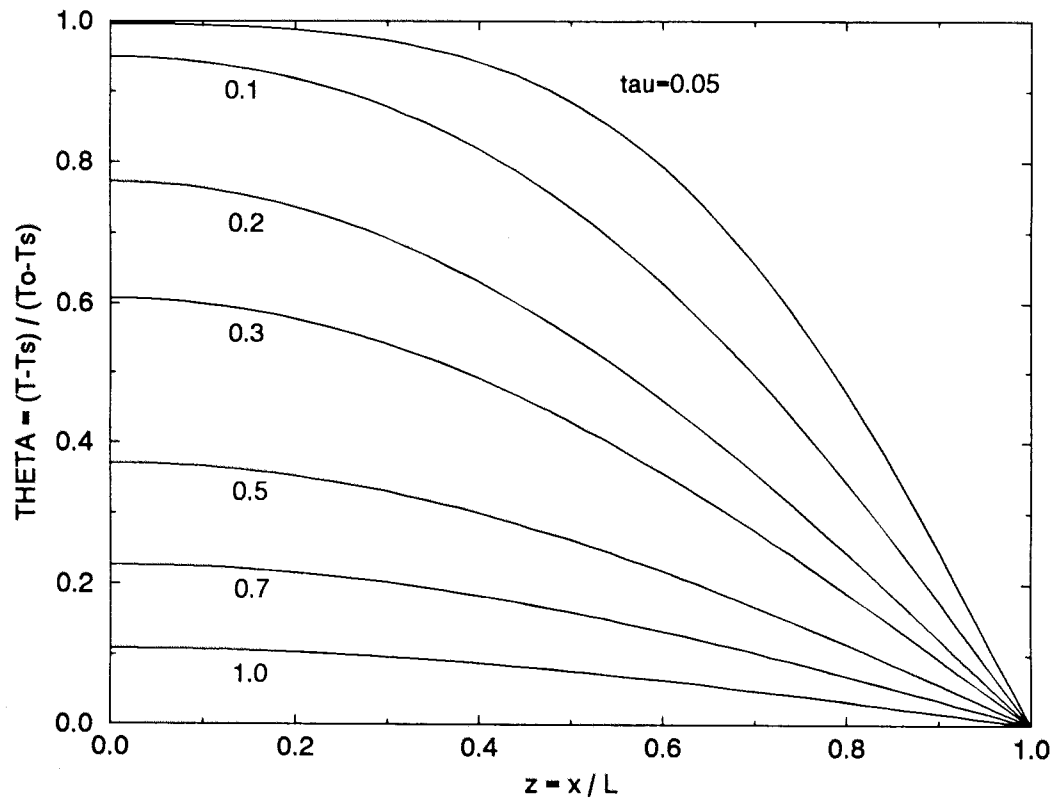   14:24 Thursday, September 16, 1993

        Parameter   Estimate   Asymptotic   Asymptotic 95 %
                                    Std. Error   Confidence Interval
                                                         Lower   Upper
        ALPHA   0.0018637419 0.00001078629 0.00184251580 0.00188496797

                    Asymptotic Correlation Matrix

                    Corr   ALPHA
                    -
                        ALPHA   1

Figure 1. Temperature Profiles for Unsteady-State Heat Conduction in a Wood Chip
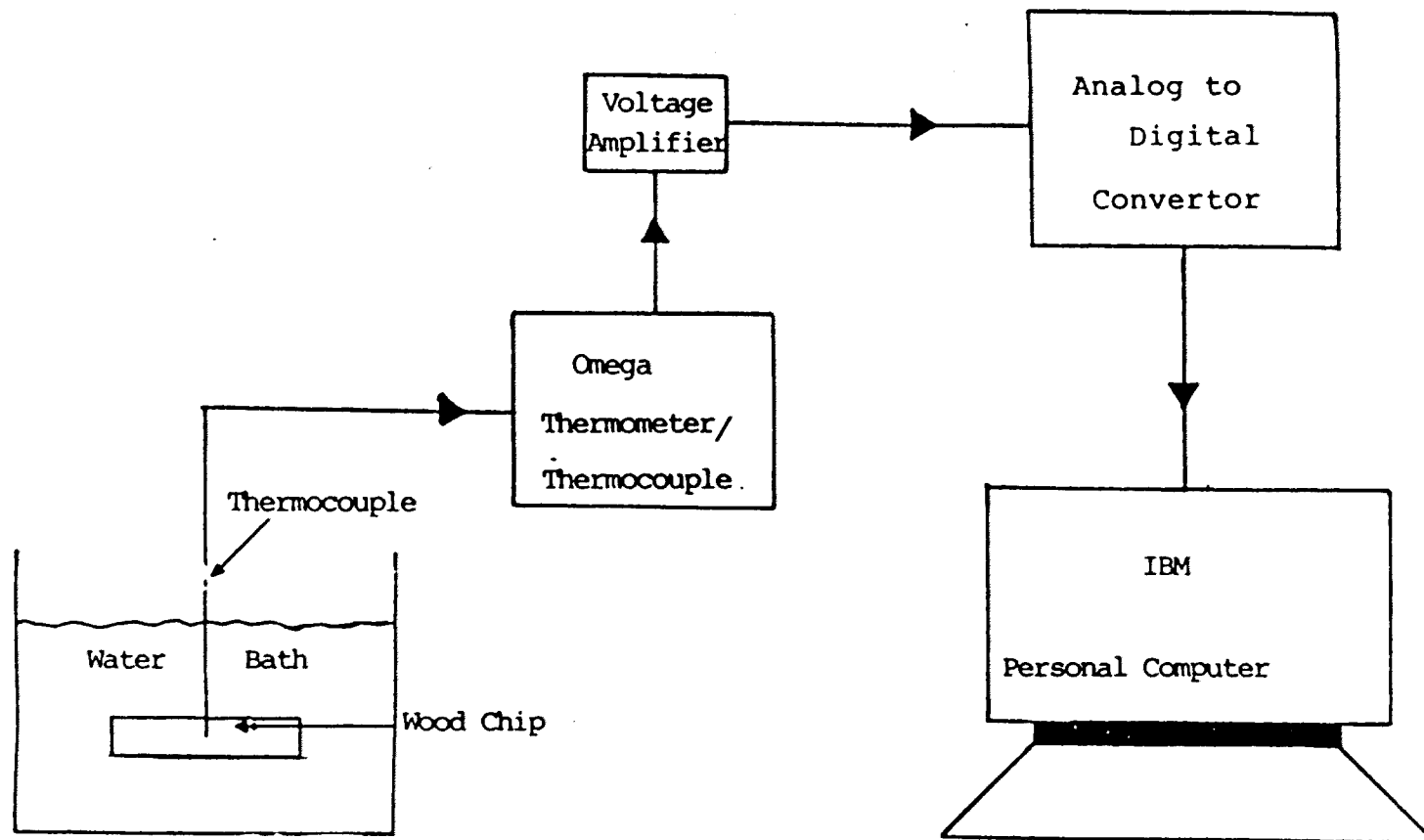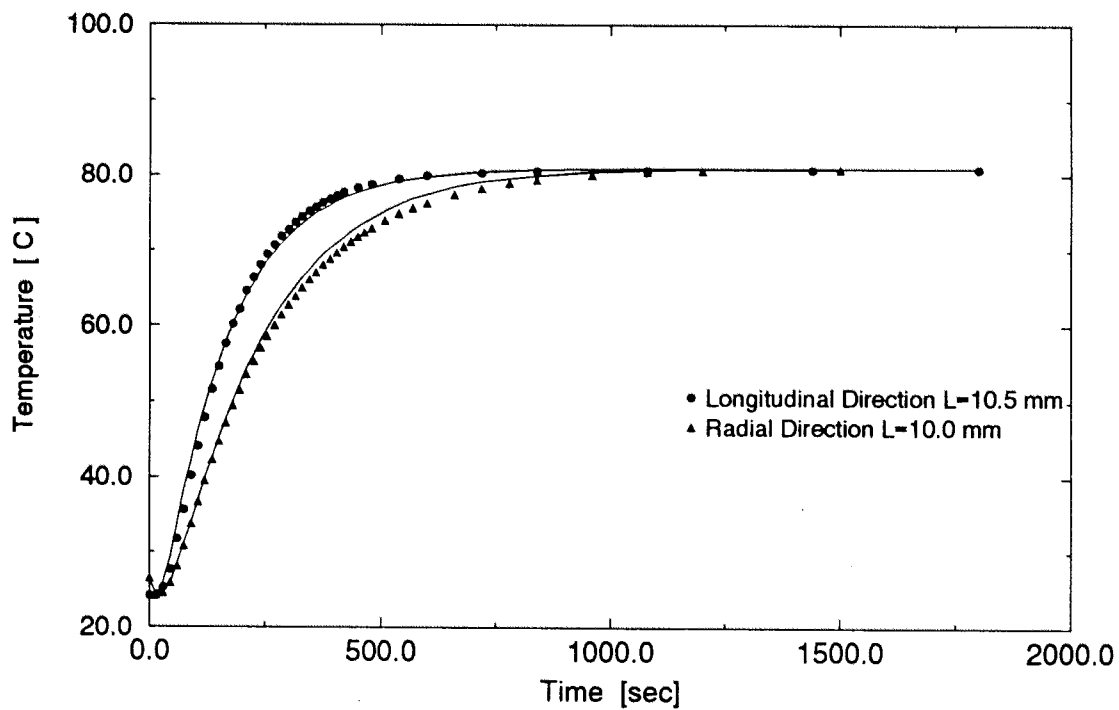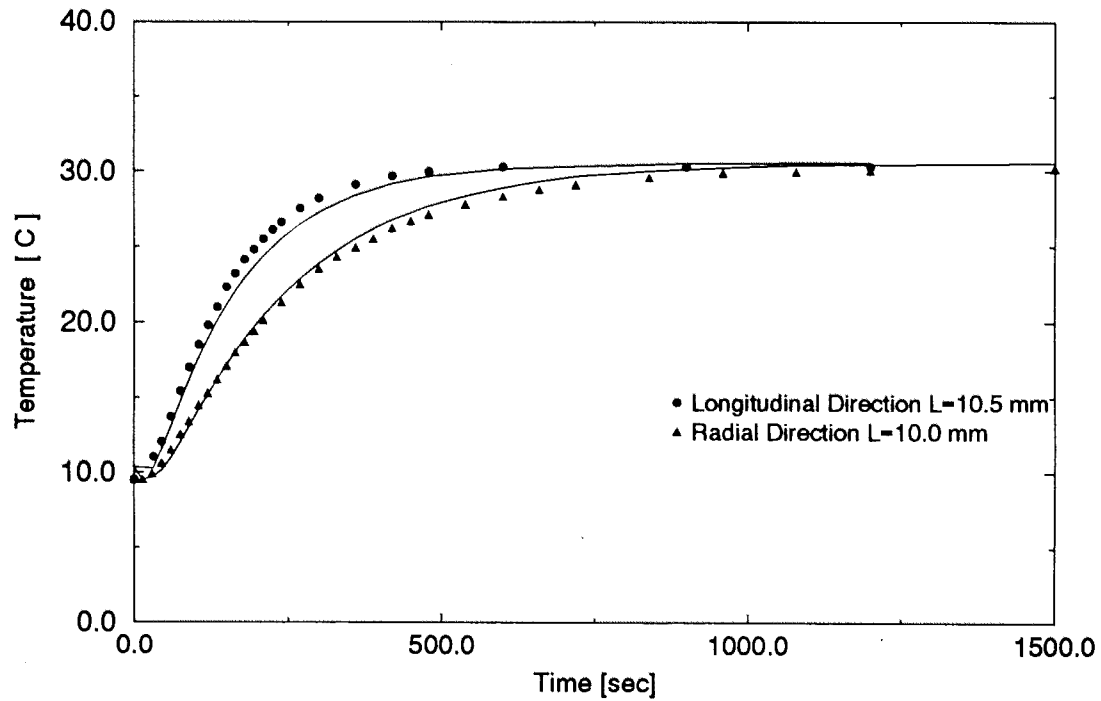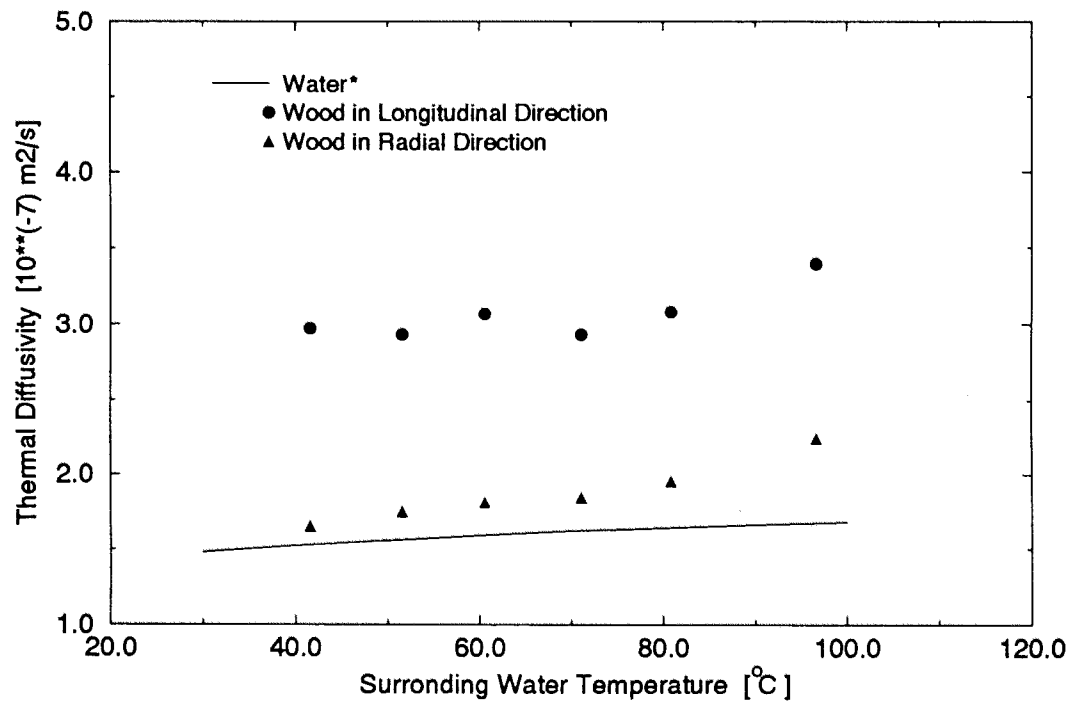
Figure 2. Schematics of the Experimental Setup

Figure 3. Temperature Profiles at the Centers of Wood Chips

(--: Best Fit for Individual Run)

Figure 4. Temperature Effect on Thermal Diffusivity

(*: Data calculated from Handbook of Chemistry and Physics, CRC press, 58th Edition, 1977-1988)